THE RATE AND MECHANISM OF THE PARTIAL OXIDATION OF ACETALDEHYDE BY PPM CONCENTRATIONS OF NITROGEN DIOXIDE

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ABSTRACT

The thermal reaction between nitrogen dioxide and acetaldehyde in the gas phase was investigated at room temperature and atmospheric pressure. The initial rate of disappearance of nitrogen dioxide was 1.00 $\pm$ 0.03 order with respect to nitrogen dioxide and 1.00 $\pm$ 0.07 order with respect to acetaldehyde. An initial second-order rate constant of (8.596 $\pm$ 0.189) x 10^{-3} $l.mole^{-1}$ sec^{-1} was obtained at 22.0 $\pm$ 0.1 ^{o}C and a total pressure of one atmosphere. The activation energy of the reaction was 12,900 cal/mole in the temperature range between 22^{o}C and 122^{o}C.

The products of the reaction were nitric oxide, carbon dioxide, methyl nitrite, nitromethane and a trace amount of trans-dimeric nitrosomethane. The addition of nitric oxide increased the rate of formation of nitromethane and decreased the rate of formation of methyl nitrite. There were no measurable surface effects due to the addition of glass wool or glass beads to the reactor.

Reactants and products were analyzed by gas chromatography. A mechanism was proposed incorporating the principal features of the reaction.

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I. INTRODUCTION

A. Oxides of Nitrogen

Air pollution in metropolitan areas is an increasing problem. Nitrogen oxides and hydrocarbons, mainly produced by automobile engines and industrial facilities, are prime pollutants. The oxides of nitrogen, hydrocarbons, ozone, and oxygen photochemically form the principal constituents of smog. The undesirable effects of photochemical smog include eye irritation, reduced visibility, oxidant formation and plant damage. The basic chemical reactions that occur in the atmosphere are not fully understood.

The reactions between the oxides of nitrogen and hydrocarbons are of great importance in other kinetic investigations. The mechanisms of the reactions of the nitrogen oxides and hydrocarbon radicals are essential for the interpretation of the kinetics of the inhibition of hydrocarbon pyrolysis, oxidation and photochemical decomposition. The reactions are also of intrinsic interest in the studies of oxidation, nitration and combustion in the gas phase.

In 1936 Staveley and Hinshelwood[56] found that nitric oxide inhibited the thermal decomposition of paraffins. Hinshelwood and other investigators[53,55] ascribed

this inhibition to the ability of nitric oxide to terminate the chain reaction by combining with the chain-propagating radicals. They concluded that the residual reaction in the presence of nitric oxide was the intramolecular, non-chain decomposition. In subsequent years the effect of nitric oxide on the thermal and photolytic decomposition of many organic compounds was investigated. This work has been summarized by Gowenlock[25].

Nitrogen dioxide received very little attention as an oxidizing agent of organic compounds in the gas phase. The addition of small quantities of nitrogen dioxide significantly affected the kinetics of the oxidation and pyrolysis of hydrocarbons. The mechanism was very complex due to the large number of reactions possible between the nitrogen oxides and organic radicals.

The partial oxidation of acetaldehyde by nitrogen dioxide was of particular interest. The reaction between acetaldehyde and nitrogen dioxide involved the principal oxides of nitrogen, nitric oxide and nitrogen dioxide, and the elementary organic radicals, methyl, methoxy and acetyl. The acetaldehyde-nitrogen dioxide reaction in the gas phase proceeded thermally and photochemically at low temperature. Therefore, the reaction provided a means to investigate the basic reactions between the nitrogen oxides and the elementary organic radicals at room temperature. The dif-

ferences between the thermal and photochemical reactions could also be considered.

In 1949 McDowell and Thomas[38,39] found that the low temperature oxidation of acetaldehyde in the gas phase was inhibited by small quantities of nitrogen dioxide. Consequently, they[40] investigated the thermal reaction between acetaldehyde and nitrogen dioxide in the gas phase above 120°C. Thomas[59] modified their acetaldehyde-nitrogen dioxide mechanism after studying the reaction between nitrogen dioxide and glyoxal. Pedlar and Pollard[47] identified nitric oxide and carbon dioxide as the principal products of the reaction between acetaldehyde and nitrogen dioxide, and proposed secondary reactions between the oxides of nitrogen and organic radicals. Christie and Voisey[20] determined an initial rate expression for the disappearance of nitrogen dioxide and postulated reactions between methyl, methoxy and acetyl radicals with nitric oxide and nitrogen dioxide. Above 100°C, Browning[9] investigated the acetaldehyde-nitrogen dioxide reaction and found nitric oxide, carbon dioxide, nitromethane, methyl nitrite and methyl nitrate as products. Phillips and Shaw[49] used acetaldehyde as a source of organic radicals, and studied the *reactions* between methyl and methoxy radicals with nitric oxide and nitrogen dioxide. At 50°C and 90°C, they identified nitric oxide, carbon dioxide, nitromethane, methyl nitrite and

methyl nitrate as products of the reactions.

The photolysis of acetaldehyde and nitrogen dioxide in the gas phase was investigated by Avery and Cvetanovic[3]. The major products of the reaction at room temperature were carbon dioxide, nitromethane, methyl nitrite and methyl nitrate. Allen and Bagley[1] also studied the photochemical reaction and identified carbon dioxide, nitromethane, methyl nitrate and methyl acetate as the principal products of the reaction at room temperature.

B. Objective

A study of the thermal reaction between acetaldehyde and nitrogen dioxide at room temperature in the gas phase was proposed after consideration of the inconsistencies in the literature for the rate of reaction, reaction mechanism and products of the reaction. The object of the experiment was to obtain concentration as a function of time data for all reactants and products. The rate of reaction, reaction mechanism, order of the reaction,and product distribution could be determined from the basic concentration-time data. The effect of surface on the reaction was to be examined by the addition of glass wool and glass beads to the reactor. The effect of temperature on the initial rate constant was to be studied in the temperature range from 20°C to 120°C. Ideally the concentrations of reactants and products could be predicted as functions of time for all

initial conditions.

II. LITERATURE

The reaction between acetaldehyde and nitrogen dioxide was investigated in the literature. The reactions between methyl, methoxy and acetyl radicals with nitric oxide and nitrogen dioxide were also examined.

A. Acetaldehyde-Nitrogen Dioxide Reaction

McDowell and Thomas[40] investigated the thermal reaction between acetaldehyde and nitrogen dioxide in the gas phase. The reaction was studied in the temperature range of 118 to 143°C, with nitrogen dioxide pressure from 11.7 to 47.7 mm Hg and acetaldehyde pressure from 57.7 to 132.8 mm Hg. The disappearance of nitrogen dioxide was measured by a photoelectric method. The rate of reaction of nitrogen dioxide was first-order with respect to acetaldehyde and nitrogen dioxide. A second-order rate constant of $10^{9.85}$ exp(-16,000/RT) $l.mole^{-1}sec^{-1}$ was determined. They concluded that nitrogen dioxide was converted to nitric oxide, and that acetaldehyde was oxidized to acetic acid. The following reaction mechanism was proposed:

$$CH_3CHO + NO_2 \longrightarrow CH_3CO + HNO_2 \qquad (1)$$

$$CH_3CO + NO_2 \longrightarrow CH_3CO_2 + NO \qquad (2)$$

$$CH_3CO_2 + HNO_2 \longrightarrow CH_3CO_2H + NO_2 \qquad (3)$$

McDowell and Thomas stated that nitrogen dioxide did not inhibit the oxidation of acetaldehyde by oxygen. They postulated that the acetaldehyde-nitrogen dioxide reaction produced nitric oxide which formed a relatively stable compound with the acetyl radical.

Based on the results of the thermal reaction between glyoxal and nitrogen dioxide, Thomas[59] modified the acetaldehyde-nitrogen dioxide mechanism:

$$CH_3CHO + NO_2 \longrightarrow CH_3CO + HNO_2 \quad (4)$$

$$CH_3CO + NO_2 \longrightarrow CH_3CO_2 + NO \quad (5)$$

$$CH_3CO_2 + CH_3CHO \longrightarrow CH_3CO_2H + CH_3CO \quad (6)$$

$$CH_3CO + NO_2 \longrightarrow \text{inert products} \quad (7)$$

$$2\ HNO_2 \longrightarrow H_2O + NO + NO_2 \quad (8)$$

The rate expression for the disappearance of nitrogen dioxide from this mechanism was first-order with respect to acetaldehyde and nitrogen dioxide.

Pedlar and Pollard[47] examined the thermal reaction between acetaldehyde and nitrogen dioxide between 110 and 180°C. The acetaldehyde pressure varied from 54 to 273 mm Hg with nitrogen dioxide pressure near 50 mm Hg. Photometric measurements of nitrogen dioxide were made through-

out the reaction. The rate of disappearance of nitrogen dioxide was first-order in acetaldehyde and first-order in nitrogen dioxide. A second-order rate constant of $10^{8.28}$ exp(-15,200/RT) $1.mole^{-1}sec^{-1}$ was reported.

The principal gaseous products were nitric oxide and carbon dioxide, with trace amounts of carbon monoxide, nitrous oxide and nitrogen. A large fraction of the initial nitrogen dioxide was not accountable in these products. No change in reaction was found for the reactor packed with glass wool. Addition of nitric oxide had no pronounced effect on the rate of reaction. Nitric oxide caused a slight inhibiting effect at high pressures of acetaldehyde which they attributed to a reaction between acetaldehyde and nitric oxide to form nitrous oxide. They proposed the following mechanism:

$$CH_3CHO + NO_2 \longrightarrow CH_3CHO\text{-}NO_2 \quad (9)$$

$$CH_3CHO\text{-}NO_2 \longrightarrow CH_3CO + HNO_2 \quad (10)$$

$$CH_3CO + NO_2 \longrightarrow CH_3CO(ONO) \quad (11)$$

$$CH_3CO(ONO) \longrightarrow CH_3 + CO_2 + NO \quad (12)$$

$$CH_3CO + NO_2 \longrightarrow CH_3CO_2 + NO \quad (13)$$

$$CH_3CO_2 \longrightarrow CH_3 + CO_2 \quad (14)$$

$$CH_3 + NO_2 \longrightarrow CH_3NO_2 \quad (15)$$

$$CH_3 + NO_2 \longrightarrow CH_3ONO \qquad (16)$$

$$2\ HNO_2 \rightleftharpoons H_2O + NO + NO_2 \qquad (17)$$

Based on the literature, Pedlar and Pollard concluded that the fraction of the initial nitrogen dioxide not accountable as nitric oxide, nitrous oxide and nitrogen, appeared as nitromethane, methyl nitrite and methyl nitrate.

Christie and Voisey[20] reported a second-order rate constant of $10^{6.2}$ exp(-12,600/RT) $l.mole^{-1}sec^{-1}$ for the rate of disappearance of nitrogen dioxide in the reaction between acetaldehyde and nitrogen dioxide. The reaction was investigated in the temperature range between 20 and 80°C, with acetaldehyde pressure from 50 to 300 mm Hg, and nitrogen dioxide pressure between 1 and 4 mm Hg. The rate of disappearance of nitrogen dioxide was first-order in acetaldehyde and first-order in nitrogen dioxide.

The results of Browning[9] were quoted by several authors[3,20,27,47]. Browning studied the thermal acetaldehyde-nitrogen dioxide reaction in the temperature range between 100 and 140°C. The rate of consumption of nitrogen dioxide was first-order with respect to acetaldehyde and nitrogen dioxide. A second-order rate constant of 10^7 exp(--13,500/RT) $l.mole^{-1}sec^{-1}$ was reported. The principal products were nitric oxide, carbon dioxide,

nitromethane, methyl nitrite and methyl nitrate.

Phillips and Shaw[49] investigated the reaction between methyl and methoxy radicals with nitric oxide and nitrogen dioxide. Quantitative analysis of the reaction products was accomplished with a infrared spectrophotometer, gas chromatograph and mass spectrometer. The acetaldehyde-nitrogen dioxide reaction was used as a source of organic radicals. The reaction was studied between 50 and 90°C, with acetaldehyde pressure from 8.9 to 116 mm Hg and nitrogen dioxide pressure between 35 and 200 mm Hg. The products were carbon dioxide, nitric oxide, nitromethane, methyl nitrite, methyl nitrate and nitrogen. They proposed the following mechanism for the reaction between acetaldehyde and nitrogen dioxide:

$$CH_3CHO + NO_2 \longrightarrow HNO_2 + CH_3CO \quad (18)$$

$$CH_3CO + NO_2 \longrightarrow CH_3CO_2 + NO \quad (19)$$

$$CH_3CO_2 \longrightarrow CH_3 + CO_2 \quad (20)$$

$$CH_3 + NO_2 \longrightarrow CH_3NO_2 \quad (21)$$

$$CH_3 + NO_2 \longrightarrow CH_3O + NO \quad (22)$$

$$CH_3O + NO \longrightarrow CH_3ONO \quad (23)$$

$$CH_3O + NO_2 \longrightarrow CH_3ONO_2 \quad (24)$$

$$CH_3 + NO_2 \longrightarrow CH_3ONO \quad (25)$$

$$CH_3 + NO \longrightarrow CH_3NO \quad (26)$$

$$CH_3NO + NO_2 \longrightarrow CH_3NO_2 + NO \quad (27)$$

$$CH_3NO + 2\ NO \longrightarrow CH_3N(NO)ONO \quad (28)$$

$$CH_3N(NO)ONO \longrightarrow CH_3 + N_2 + NO_3 \quad (29)$$

$$NO_3 + NO \longrightarrow 2\ NO_2 \quad (30)$$

The photochemical reaction between acetaldehyde and nitrogen dioxide in the gas phase at room temperature was studied by Allen and Bagley[1]. At 25°C and with 3660 Å irradiation, the products of the reaction were carbon dioxide, nitromethane, methyl nitrate and methyl acetate. No methyl nitrite was identified.

Avery and Cvetanovic[3] also investigated the photolysis of acetaldehyde in the presence of nitrogen dioxide at room temperature. The pressure of nitrogen dioxide was 1.45 mm Hg and the pressure of acetaldehyde was 10.0 mm Hg. The major products of the reaction were carbon dioxide, nitromethane, methyl nitrite and methyl nitrate.

B. Acetyl Radical-Nitrogen Dioxide Reaction

The acetyl radical was reported to be stable at room temperature. O'Neal and Benson[45] observed the thermal decomposition of the acetyl radical to form a methyl radical and carbon monoxide above 200°C:

$$CH_3CO \longrightarrow CH_3 + CO \qquad (31)$$

Anderson and Rollefson[2] and Herr and Noyes[28] found evidence of the thermal decomposition of the acetyl radical above 60°C.

Investigators reported that the reaction between the acetyl radical and nitrogen dioxide produced a methyl radical, nitric oxide and carbon dioxide. McDowell and Thomas[40] suggested the acetyloxy intermediate, CH_3CO_2[52]:

$$CH_3CO + NO_2 \longrightarrow CH_3CO_2 + NO \qquad (32)$$

$$CH_3CO_2 \longrightarrow CH_3 + CO_2 \qquad (33)$$

Pedlar and Pollard[47] postulated the acetyl nitrite intermediate, $CH_3CO(ONO)$:

$$CH_3CO + NO_2 \longrightarrow CH_3CO(ONO) \qquad (34)$$

$$CH_3CO(ONO) \longrightarrow CH_3 + CO_2 + NO \qquad (35)$$

Christie and Voisey[19] found that the acetyl radical-nitrogen dioxide reaction proceeded five times faster than the corresponding acetyl radical-nitric oxide reaction in the temperature range from 20 to 80°C. They concluded that the reaction between the acetyl radical and nitrogen di-

oxide was the chain-terminating step in the disproportionation of nitric oxide by acetyl radicals.

C. Acetyl Radical-Nitric Oxide Reaction

Several authors[2,16,19,30] postulated the formation of the 2-nitrosoethan-2-al, $CH_3CO(NO)$, intermediate from the reaction between nitric oxide and the acetyl radical:

$$CH_3CO + NO \longrightarrow CH_3CO(NO) \qquad (36)$$

Christie, Collins and Voisey[16] found that acetyl radicals catalyzed the disproportionation of nitric oxide to nitrogen dioxide and nitrogen:

$$4\ NO \longrightarrow 2\ NO_2 + N_2 \qquad (37)$$

They proposed the following mechanism involving the 2-nitrosoethan-2-al intermediate:

$$CH_3CO + NO \longrightarrow CH_3CO(NO) \qquad (38)$$

$$CH_3CO(NO) + 2\ NO \longrightarrow CH_3CO + N_2 + NO_3 \qquad (39)$$

$$NO_3 + NO \longrightarrow 2\ NO_2 \qquad (40)$$

Christie and Voisey[19] reported that the disproportionation of nitric oxide by acetyl radicals proceeded twenty

times faster than the corresponding disproportionation of nitric oxide by methyl radicals.

D. Methyl Radical-Nitrogen Dioxide Reactions

Gray[27] examined the reactions that were possible between methyl radicals and nitrogen dioxide from theoretical considerations and qualitative data from the literature. He concluded that three different products were possible for the reaction between a methyl radical and nitrogen dioxide:

$$CH_3 + NO_2 \longrightarrow CH_3NO_2 \qquad (41)$$

$$CH_3 + NO_2 \longrightarrow CH_3ONO \qquad (42)$$

$$CH_3 + NO_2 \longrightarrow CH_3O + NO \qquad (43)$$

Gray postulated that only reactions (41) and (43) were possible in the gas phase, and reaction (42) was improbable except at high third-body pressures.

Patsevich, Topchiev and Shtern[46] disagree with the conclusions reached by Gray. They investigated the reactions between methyl radicals and nitrogen dioxide in the temperature range from -15 to 96°C. The total pressure was less than 3 mm Hg and the pressure of nitrogen dioxide was 0.08 mm Hg. They found that methyl nitrite was produced by reaction (42) at room temperature by the direct

association of nitrogen dioxide and a methyl radical. Nitromethane was formed faster than methyl nitrite. A ratio of the rate constants k_{41}/k_{42} of 3 was obtained at room temperature. Reaction (43), the formation of a methoxy radical and nitric oxide, did not occur below 100°C. Patsevich, Topchiev and Shtern found that the methyl radical-nitrogen dioxide reactions were not affected by surface factors.

Rebbert and Slagg[51] also examined the reactions between nitrogen dioxide and the methyl radical. They observed reactions (41), (42) and (43) at room temperature. The photolysis of azomethane in the presence of small amounts of nitrogen dioxide yielded a ratio of the rate constants k_{41}/k_{42} of 8 at 30°C, but they found the ratio was pressure dependent. Rebbert and Slagg reported that $k_{41}/(k_{42} + k_{43}) = 0.42$ at 25°C but they assumed that nitric oxide reacted only with methoxy radicals to form methyl nitrite.

Phillips and Shaw[49] used the acetaldehyde-nitrogen dioxide reaction as a source of organic radicals in their studies of the reactions of nitric oxide and nitrogen dioxide. They observed reactions (41) and (43) at 50°C and 90°C, but concluded reaction (42) was insignificant in the production of methyl nitrite. A ratio of the rate constants $k_{41}/k_{43} = 0.5$ was reported at 90°C.

E. Methyl Radical-Nitric Oxide Reaction

The reaction between nitric oxide and methyl radicals to form nitrosomethane was studied by several investigators.

$$CH_3 + NO \longrightarrow CH_3NO \qquad (44)$$

A second-order rate constant was obtained by Forsyth[24] of 1.1×10^7 $l.mole^{-1}sec^{-1}$ at 800°C, by Miller and Steacie[42] of 3.1×10^6 $l.mole^{-1}sec^{-1}$ at 27°C, by Durham and Steacie[23] of 3.3×10^7 $l.mole^{-1}sec^{-1}$ at 325°C, by Lossing, Ingold and Tickner[36] of $3\text{-}6 \times 10^7$ $l.mole^{-1}sec^{-1}$ at 950°C, by Bryce and Ingold[11] of 1.3×10^8 $l.mole^{-1}sec^{-1}$ at 480°C and 1.4×10^8 $l.mole^{-1}sec^{-1}$ at 900°C, by Birss, Danby and Hinshelwood[6] of $0.6\text{-}2.0 \times 10^7$ $l.mole^{-1}sec^{-1}$ at 160°C, by Christie[14] of 7×10^8 $l.mole^{-1}sec^{-1}$ at 20°C, by Sleppy and Calvert[54] of 1.05×10^9 $l.mole^{-1}sec^{-1}$ at 25°C and by Hoare[30] of 2.2×10^9 $l.mole^{-1}sec^{-1}$ at 200°C.

There was considerable controversy concerning the pressure region where the transition from third-order kinetics, third-body dependent, to second-order kinetics occurred. Hoare[30] observed third-order kinetics at 200°C and a total pressure of 200 mm Hg. Christie[14], Sleppy and Calvert[54] and Phillips and Shaw[49] reported second-order kinetics above 100°C and a total pressure of 100 mm

Hg.

Nitrosomethane, the product of the combination of a methyl radical and nitric oxide at low temperature, was identified by long-path infrared spectrophotometry by Calvert, Thomas and Hanst[12]. Maschke, Shapiro and Lampe[37] used a mass spectrometer to identify nitrosomethane.

Various investigators reported the isomerization and subsequent decomposition of nitrosomethane at temperatures above 200°C:

$$CH_3 + NO \longrightarrow CH_3NO \quad (45)$$

$$CH_3NO \longrightarrow CH_2NOH \quad (46)$$

$$CH_2NOH \longrightarrow OHCNH_2 \quad (47)$$

$$CH_2NOH \longrightarrow HCN + H_2O \quad (48)$$

$$OHCNH_2 \longrightarrow NH_3 + CO \quad (49)$$

Raley, Rust and Vaughan[50] isolated formaldoxime, CH_2NOH, as a product of the reaction between methyl radicals and nitric oxide at 225°C. Batt and Gowenlock[4] observed a first-order reaction for the disappearance of nitrosomethane in the gas phase from 250 to 400°C, and proposed that formaldoxime was the product. Taylor and Bender[58] investigated the thermal decomposition of formaldoxime from

350 and 415°C and identified water, hydrogen cyanide, carbon monoxide and ammonia as products of the decomposition. In the temperature range from 480 to 900°C, Bryce and Ingold[11] also reported water, hydrogen cyanide, carbon monoxide and ammonia as the products of the reaction between methyl radicals and nitric oxide.

When there was a large excess of methyl radicals compared to the number of molecules of nitric oxide, nitrosomethane was not the final product of the methyl radical-nitric oxide reaction. The nitrosomethane reacted with two methyl radicals to form trimethylhydroxylamine, $(CH_3)_2NOCH_3$:

$$CH_3 + NO \longrightarrow CH_3NO \qquad (50)$$

$$CH_3NO + 2\ NO \longrightarrow (CH_3)_2NOCH_3 \qquad (51)$$

Hoare[30] found that three methyl radicals could be removed per nitric oxide molecule from experiments at 200°C. He concluded that trimethylhydroxylamine was produced by the addition of two methyl radicals across the double bond in nitrosomethane. Bromberger and Phillips[7] and Phillips [48] identified trimethylhydroxylamine by gas chromatography and mass spectroscopy as a product of the reaction between methyl radicals and nitrosomethane. Maschke, Shapiro and

Lampe[37] investigated the reactions of excess CD_3 radicals with nitric oxide. They found that the CD_3 radicals reacted with nitric oxide to form CD_3NO until all the molecules of nitric oxide were consumed. The excess CD_3 radicals then attacked the CD_3NO to form $(CD_3)_2NOCD_3$. They concluded that nitric oxide was fifteen times more effective than nitrosomethane in scavenging methyl radicals.

When the concentration of nitric oxide was very much greater than the concentration of methyl radicals, the methyl radicals catalyzed the disproportionation of nitric oxide to nitrogen dioxide and nitrogen:

$$4\ NO \longrightarrow 2\ NO_2 + N_2 \qquad (52)$$

Christie and co-workers[15,17,18] offered the following mechanism for the disproportionation of nitric oxide by methyl radicals:

$$CH_3 + NO \longrightarrow CH_3NO \qquad (53)$$

$$CH_3NO + 2\ NO \longrightarrow CH_3N(ONO)NO \qquad (54)$$

$$CH_3N(ONO)NO \longrightarrow CH_3N_2NO_3 \qquad (55)$$

$$CH_3N_2NO_3 \longrightarrow CH_3 + N_2 + NO_3 \qquad (56)$$

$$NO_3 + NO \longrightarrow 2\ NO_2 \qquad (57)$$

The first reaction was the formation of nitrosomethane from methyl radicals and nitric oxide. The nitrosomethane reacted with two molecules of nitric oxide to form the intermediate N-methyl-N-nitrosohydroxylamine nitrite, $CH_3N(ONO)NO$. The N-alkyl-N-nitrosohydroxylamine nitrite was proposed as the intermediate in the reactions of C-nitroso-compounds with excess nitric oxide by Brown[8], Burrell[10], Donaruma and Carmody[22], Strausz and Gunning[57] and Batt and Gowenlock[4]. The N-methyl-N-nitrosohydroxylamine nitrite cyclized and formed the unstable methyl diazonium nitrate, $CH_3N_2NO_3$. The methyl diazonium nitrate decomposed and produced nitrogen and nitrogen trioxide and regenerated the methyl radical. The nitrogen trioxide reacted with excess nitric oxide to form nitrogen dioxide. The over-all reaction was the formation of two moles of nitrogen dioxide and one mole of nitrogen from four moles of nitric oxide.

Christie[15] obtained a third-order rate constant of 55 $l.^2mole^{-2}sec^{-1}$ at 25°C for the reaction between nitrosomethane and nitric oxide. The reaction was first-order with respect to nitrosomethane and second-order with respect to nitric oxide. Johnston and Heicklen[31] found a third-order rate constant of 47 $l.^2mole^{-2}sec^{-1}$ at room temperature for the nitrosomethane-nitric oxide reaction.

Christie, Frost and Voisey[17] determined an expression of 2.6 exp(1800/RT) $1.^2 mole^{-2} sec^{-1}$ for the third-order rate constant between 25 and 70°C. The reaction was first-order in nitrosomethane and second-order in nitric oxide. The rate constant was found to decrease with an increase in temperature.

Johnston and Heicklen[31] reported a reaction between nitrosomethane and nitric oxide which was first-order in nitrosomethane and first-order in nitric oxide:

$$CH_3NO + NO \longrightarrow CH_3O + N_2O \qquad (58)$$

They investigated the photolysis of methyl iodide in the presence of nitric oxide at room temperature, and identified nitrous oxide as a secondary product of the reaction. They obtained a second-order rate constant of 0.017 $l.mole^{-1}sec^{-1}$ at room temperature for reaction (58).

F. Nitrosomethane Dimerization

Several authors have reported the dimerization of nitrosomethane at room temperature:

$$2\ CH_3NO \rightleftharpoons (CH_3NO)_2 \qquad (59)$$

$$\text{gas}\ (CH_3NO)_2 \longrightarrow (CH_3NO)_2\ \text{solid} \qquad (60)$$

Thompson and Linnet[60] observed the formation of a white solid during the photolysis of mercury dimethyl in the presence of nitric oxide at room temperature. Coe and Doumani[21] identified a stable dimer of nitrosomethane at 25°C. The nitrosomethane dimer formed long colorless needles on the surface of their quartz reactor. Chilton, Gowenlock and Trotman[13] isolated two forms of the dimer of nitrosomethane in the temperature range from 330 to 390°C. Gowenlock and Trotman[26] characterized the properties of the cis- and trans-dimers of nitrosomethane.

A second-order rate constant for the dimerization of nitrosomethane was obtained by Christie[15] of 12 $l.mole^{-1}$ sec^{-1} at 25°C, by Christie, Frost and Voisey[17] of 25 $l.mole^{-1}sec^{-1}$ at 25°C, by Johnston and Heicklen[31] of 71 $l.mole^{-1}sec^{-1}$ at 25°C, and by Calvert, Thomas and Hanst[12] of 71 $l.mole^{-1}sec^{-1}$ at 25°C. Christie, Frost and Voisey also determined an expression for the second-order rate constant of $10^{5.1}$ $\exp(-4600/RT)$ $l.mole^{-1}sec^{-1}$ in the temperature range of 25 to 75°C.

Batt, Gowenlock and Trotman[5] measured the thermal decomposition of the dimer of nitrosomethane. They obtained an expression for the first-order decomposition of 10^{12} $\exp\{(-22{,}200 \pm 2{,}000)/RT\}$ sec^{-1} in the temperature range between 100 and 130°C. Christie, Frost and

Voisey[17] determined a first-order rate expression of $10^{11.2}$ exp(-20,600/RT) sec^{-1} between 20 and 75°C for the thermal decomposition of the dimer of nitrosomethane.

G. Methoxy Radical-Nitrogen Dioxide Reaction

Methoxy radicals were produced in reaction (43) by the oxidation of methyl radicals with nitrogen dioxide:

$$CH_3 + NO_2 \longrightarrow CH_3O + NO \qquad (43)$$

Investigators found that the reaction between methoxy radicals and nitrogen dioxide produced methyl nitrate:

$$CH_3O + NO_2 \longrightarrow CH_3ONO_2 \qquad (61)$$

Phillips and Shaw[49] reported that methoxy radicals reacted faster with nitrogen dioxide than with nitric oxide They obtained a ratio of the rate constants of k_{61}/k_{62} = 1.8 at 90°C. Johnston and Heicklen[31] also found that methoxy radicals reacted faster with nitrogen dioxide than with nitric oxide. They determined a value of k_{61}/k_{62} = 1.4 at 25°C for the ratio of the relative rate constants.

H. Methoxy Radical-Nitric Oxide Reaction

Knight and Gunning[32] found that methyl nitrite was

the product of the reaction between methoxy radicals and nitric oxide:

$$CH_3O + NO \longrightarrow CH_3ONO \qquad (62)$$

Most investigators[9,27,31,49] concluded that methyl nitrite was only produced by reaction (62) by the combination of methoxy radicals with nitric oxide. Other authors[46,51] reported that methyl nitrite was solely formed by reaction (42) by the direct association of methyl radicals and nitrogen dioxide:

$$CH_3 + NO_2 \longrightarrow CH_3ONO \qquad (42)$$

The mechanism of the formation of methyl nitrite was a function of the temperature and pressure of the reaction, and the organic radicals that were present.

I. Summary of the Literature

The following statements about the reaction between acetaldehyde and nitrogen dioxide can be made based upon the literature.

All investigators[9,40,47] studied the reaction at temperatures above 100°C and total pressures below one

atmosphere. The concentration of nitrogen dioxide was monitored continuously during the reaction. The products were determined quantitatively at the conclusion of the reaction.

The rate of reaction of nitrogen dioxide[9,20,40,47] was first-order with respect to acetaldehyde and nitrogen dioxide. Second-order rate constants that ranged between 10^{-4} to 10^{-2} $l.mole^{-1}sec^{-1}$ at 25°C were reported. The activation energy of the reaction between acetaldehyde and nitrogen dioxide varied between 12,600 and 16,000 cal/mole in the different experiments. Only two investigators[46,47] considered the influence of surface on the reaction, and they found no measurable effect.

The majority of investigators identified nitric oxide[9,40,47,49] and carbon dioxide[1,3,9,47,49] as the principal products of the acetaldehyde-nitrogen dioxide reaction. Secondary products of the reaction that were isolated included nitromethane[1,3,9,49], methyl nitrite[3,9,49], methyl nitrate[1,3,9,49], carbon monoxide[47], nitrous oxide[47], nitrogen[47,49], acetic acid[40] and methyl acetate[1].

In conclusion, several aspects concerning the reaction between nitrogen dioxide and acetaldehyde have not been investigated. The reaction at room temperature has received very little attention. No information about the reaction at total pressures near one atmosphere is avail-

able. The concentrations of the products of the reaction have not been monitored during the reaction. No attempts have been made to obtain expressions for the concentrations of the products as functions of time. Low concentrations of nitrogen dioxide and high concentrations of acetaldehyde approximate the conditions of the pyrolysis, oxidation, and photolysis of acetaldehyde inhibited by nitrogen dioxide. Investigators have not considered the reaction of ppm concentrations of nitrogen dioxide with a large excess of acetaldehyde. The present work investigated those areas.

III. EXPERIMENTAL METHOD

A. Technique

The experiment was designed to investigate the thermal reaction between acetaldehyde and nitrogen dioxide in the gas phase. The reactions of ppm concentrations of nitrogen dioxide with a large excess of acetaldehyde were examined. A constant-volume batch reactor was used in the experiment. Total pressures of the reactor near one atmosphere and temperatures of $22 \pm 1\ ^{o}C$ were considered.

Gas chromatography was employed for the quantitative analysis of reactants and products during the reaction. An electron-capture detector was used to determine the concentrations of nitrogen dioxide, carbon dioxide, methyl nitrite and nitromethane. The concentration of acetaldehyde was determined by a hydrogen flame-ionization detector.

The reactor was sampled every ten minutes and the concentrations of the reactants and products were determined. The concentrations were obtained as functions of time during the reaction.

B. Areas of Investigation

The initial partial pressures of nitrogen dioxide and acetaldehyde were varied to study the initial rate constant for the disappearance of nitrogen dioxide, the order of the

reaction with respect to acetaldehyde and nitrogen dioxide, and the rates of formation of the products. Initial partial pressures of nitrogen dioxide varied between 0.01 and 0.03 mm Hg, and the initial partial pressures of acetaldehyde ranged from 20 to 150 mm Hg.

The effect of nitric oxide on the reaction between acetaldehyde and nitrogen dioxide was investigated by the addition of initial quantities of nitric oxide to the reaction. Initial partial pressures of nitric oxide were between 0 and 0.004 mm Hg.

Glass beads and glass wool were added to the reactor to determine the effect of surface on the reaction.

The temperature dependence of the initial rate constant and the activation energy of the reaction were studied at elevated temperatures. A series of tests were performed between 20 and 120^{o}C for this purpose.

A total of thirty tests were reported.

IV. EXPERIMENTAL APPARATUS

A. Reactor System

A schematic diagram of the reactor system is presented in Figure 1.

The constant-volume batch reactor consisted of a cylindrical vessel of Pyrex glass with a rounded top and bottom. The outside diameter of the reactor was six inches, the length was twelve inches, and the total volume was approximately three liters. Four glass tubes with thick walls entered the reactor. A glass tube with an outside diameter of 3/4-inch was located at the top of the reactor and was used to evacuate the vessel. One glass tube with an outside diameter of 3/8-inch was located at the front of the reactor, six inches from the base, and was used to add gases to the reactor. A second glass tube with an outside diameter of 3/8-inch was located on the side of the reactor, three inches from the base, and connected the reactor to a manometer to measure the pressure in the vessel. The third glass tube with an outside diameter of 3/8-inch was located on the opposite side of the reactor, also three inches from the base, and was used to withdraw gas samples from the reactor for analysis in the chromatograph.

Two mix tanks were used to dilute the pure reactants with nitrogen. For high temperature tests, the reactants

were heated in the mix tanks before addition to the reactor. The dimensions of the mix tanks were the same as the dimensions of the reactor. The four tubes were used for evacuation, pressure measurement, addition of gases to the mix tank from the cylinders, and the addition of gases to the reactor from the mix tank.

The reactor and mix tanks were connected to mercury manometers and a McLeod gauge for pressure measurements. The McLeod gauge was used to determine the vacuum pressure in the reactor and mix tanks prior to a calibration or oxidation. A cathetometer was used to measure the height of the mercury columns in the manometers.

Temperature control in the reactor enclosure was maintained by a Fisher thermoregulator. The thermoregulator was located three inches above a centrifugal fan. The centrifugal fan, with a diameter or six inches and operated at 1750 rpm, was used to circulate the air in the reactor enclosure. A 500 watt nichrome resistance heater was located at the outlet of the fan and was used for temperature control at 22.0°C. Banks of 660 watt Glo-coil heaters were employed at higher temperatures. Temperature measurements were obtained with copper-constantan thermocouples.

The reactor enclosure was a 2.5 x 3.0 x 6.5 ft Unistrut frame. The front panel was 1/8-inch aluminum, and

the remaining sides and the top were made of 1/4-inch masonite. The rectangular enclosure was insulated with Fiberglas insulation with a thickness of three inches. The reactor, mix tanks, fan, temperature controller, heaters and standard tank were located in the reactor enclosure. The McLeod gauge, three manometers and flow valves were mounted on the front panel.

A Kinney vacuum pump was used for evacuation of the reaction system below five microns. A Duo-Seal vacuum pump was employed in conjunction with the McLeod gauge and manometers. Evacuation lines were stainless steel tubing with an outside diamter of 3/4-inch, with Jamesbury ball valves and Swagelok connectors. All remaining lines were stainless-steel tubing with an outside diameter of 1/8-inch, with Whitey valves and Swagelok connectors. Glass-to-stainless steel connections were Swagelok reducing unions with nylon back ferrules and teflon front ferrules. All vessels, tubing, connectors and valves were cleaned with distilled water, acetone and methanol prior to installation. The entire system was cleaned by evacuation and heating.

B. Chromatograph Unit

A schematic diagram of the chromatography unit is presented in Figure 2.

A Loenco 160 EFX Chromatograph with a hydrogen flame-ionization detector and a modified[43] electron-capture detector was used in this study. A Loenco L-208-6 sample valve was employed with each detector to allow different carrier gases for the hydrogen flame-ionization detector and the electron-capture detector. The Hewlett-Packard 214A Pulse Generator was used in conjunction with the electron-capture detector. The signals from the detectors were monitored with Texas Instrument "servo/riter II" recorders. The recorder for the hydrogen flame-ionization detector was equiped with a disc integrator. A stainless steel cylinder with a volume of five liters was used as a standard tank for conditioning the columns.

An electron-capture detector designed by Morrison[43, 44] was used for the quantitative determination of nitrogen dioxide, carbon dioxide, methyl nitrite and nitromethane. It was also employed for the trace analysis of nitrous oxide and methyl nitrate. The operating conditions for the electron-capture detector were: (1)a detector temperature of 190°C, (2)an argon carrier gas with no scavenger gas, (3)a pulse amplitude of 8 volts, (4)a pulse width of 10 microseconds, and (5)a pulse period of 1000 microseconds. A discussion of the investigation and optimization of the electron-capture detector is presented in Appendix B.

A column was required for the separation of nitrogen, nitrogen dioxide, carbon dioxide, acetaldehyde, methyl nitrite and nitromethane. The column was twenty feet in length, with an outside diameter of 1/8-inch, and packed with ten percent by weight of SF-96 on 40/80 mesh Fluoropak 80. The operating conditions of the column were: (1)a column temperature of 22°C, (2)an argon carrier gas flow rate of 500 cc/min, and (3)a sample size of 0.5 cc. A discussion of the column development is presented in Appendix C.

The hydrogen flame-ionization detector was used for the quantitative determination of acetaldehyde. Trace analysis of organic compounds which might be products of the acetaldehyde-nitrogen dioxide reaction were also performed by the flame-ionization detector. The operating conditions of the detector were: (1)a hydrogen flow rate of 60 cc/min, (2)an air flow rate of 350 cc/min, and (3)a a detector temperature of 190°C.

A column was needed for the separation of the organic compounds which might be produced by the reaction between acetaldehyde and nitrogen dioxide. The column was twenty feet in length, with an outside diameter of 1/8-inch, and packed with 80/100 mesh Poropak Q. The operating conditions of the column were: (1)a column temperature of 180°C,

(2)a helium carrier gas flow rate of 50 cc/min, and (3)a sample size of 0.5 cc. The column development is discussed in Appendix C.

C. Chemicals

Cylinders of commercial grade hydrogen, helium and air, and high-purity dry argon (99.996 percent) and nitrogen (99.995 percent) were furnished by Linde. Matheson and Victor supplied two-stage regulators for the cylinders. Impurities in the gases were removed in tubes with lengths of one foot and inside diameters of 1/2-inch. They were packed with 13X molecular sieve. The gases were dried by passage through a coiled column which had a length of four feet, and was packed with 5A molecular sieve. The columns were located in a dry-ice-acetone slurry.

Nitrogen dioxide was obtained from a cylinder furnished by Matheson. The mixture of nitrogen dioxide in nitrogen was analyzed for nitrogen dioxide by the phenol-disulfonic acid method (ASTM D 1608-60). It was found to contain 350 ppm of nitrogen dioxide in nitrogen, and the maximum amount of impurities in the mixture was 10 ppm.

Matheson also supplied a mixture of nitric oxide in nitrogen. The mixture of nitric oxide in nitrogen was analyzed by the phenol-disulfonic acid method. The re-

sults were compared to the concentrations obtained in the oxidation of nitric oxide to nitrogen dioxide. It was found to contain 319 ppm of nitric oxide in nitrogen, and the maximum amount of impurities in the mixture was 10 ppm.

Acetaldehyde (b.p. 20-22°C) was furnished by Eastman Organic Chemicals. Purification by bulb-to-bulb distillation at reduced pressures was not necessary.

Chemicals used in the calibration of the chromatograph are listed in Appendix D.

V. EXPERIMENTAL PROCEDURE

A. Oxidation Test

In an oxidation test the two mix tanks were evacuated to pressures below 0.005 mm Hg. The mixture containing 350 ppm of nitrogen dioxide in nitrogen was added to the first mix tank and diluted with nitrogen. The mixture in the mix tank contained approximately 150 ppm of nitrogen dioxide in nitrogen. Acetaldehyde was added to the second mix tank.

After the mixtures of reactants were prepared in the mix tanks, the reactor was evacuated to a pressure below 0.005 mm Hg. Acetaldehyde was added to the reactor from the second mix tank. Nitrogen was added to the reactor to bring the total pressure of the reactor to approximately 700 mm Hg.

The chromatography columns were conditioned with samples of nitrogen dioxide and hydrocarbons from the standard tank. The responses of the electron-capture and flame-ionization detectors were also standardized.

The timer was started on the addition of the mixture of nitrogen dioxide in nitrogen from the first mix tank to the reactor. The pressure of the reactor was slightly greater than one atmosphere.

Samples were withdrawn from the reactor at intervals

of ten minutes and analyzed with the chromatograph. Temperature measurements were made every thirty minutes during a run. A normal oxidation test lasted 500 minutes.

B. Mixing of Reactants

The time required for complete mixing of the reactants was less than thirty seconds. The reactor was evacuated to a pressure below 0.005 mm Hg. Nitrogen was added to the reactor to bring the total pressure of the reactor to 700 mm Hg. A mixture containing 150 ppm of nitrogen dioxide in nitrogen was added to the reactor. The pressure of the reactor was slightly greater than one atmosphere. Thirty seconds after the addition of nitrogen dioxide, a sample was withdrawn from the reactor. Samples were taken from the reactor at five minute-intervals and analyzed with the chromatograph. The concentrations of nitrogen dioxide were the same for each sample. This result indicated complete mixing of the reactants in less than thirty seconds.

C. Analysis of the Data

The initial concentrations of nitrogen dioxide and acetaldehyde were determined assuming ideal gas behavior:

$$C_{NO_2}(t=0) = P_{NO_2}/RT \tag{63}$$

$$C_{CH_3CHO}(t=0) = P_{CH_3CHO}/RT \tag{64}$$

The concentrations of nitrogen dioxide, acetaldehyde, carbon dioxide, methyl nitrite and nitromethane, as functions of time, were determined by gas chromatography (See Appendix D for details). The concentration of nitric oxide as a function of time was determined from a material balance for nitrogen:

$$n_{NO_2}(t=0) + n_{NO}(t=0) = n_{NO_2} + n_{NO} + n_{CH_3ONO} + n_{CH_3NO_2} \quad (65)$$

where $n_i(t=0)$ is the initial number of moles of component i, and n_i is the number of moles of component i at time t.

Plots of the concentrations of nitrogen dioxide, nitric oxide, carbon dioxide, methyl nitrite and nitromethane as functions of time were prepared on 20-inch graph paper. The concentration-time data were smoother by eye for each component for two reasons. First, the concentrations of reactants and products were required as continuous functions of time. Second, it was necessary to extrapolate the concentration-time data for the products for the first points. The concentration-time data were fitted by a linear least-squares technique on the computer. The derivatives, dC_i/dt, were determined for nitrogen dioxide, nitric oxide, carbon dioxide, methyl nitrite and nitromethane.

D. Experimental Error

The sources of experimental error were (1)the phenol-disulfonic acid determinations for nitrogen dioxide and nitric oxide, (2)the ideal gas assumption for the initial concentrations of reactants, (3)the use of the mercury manometers and cathetometer to determine the initial partial pressures of nitrogen dioxide, nitric oxide and acetaldehyde, (4)the chromatographic analysis for nitrogen dioxide, carbon dioxide, methyl nitrite, nitromethane and acetaldehyde, (5)the temperature fluctuations during an oxidation test, and (6)the decrease in the total pressure of the reactor due to sampling.

A maximum error of six percent was expected for a single analysis by the phenol-disulfonic acid determination of the mixture of nitrogen dioxide in nitrogen and the mixture of nitric oxide in nitrogen. Twenty samples of the mixture of nitrogen dioxide in nitrogen and twenty samples of the mixture of nitric oxide in nitrogen were analyzed by this technique. The results for the mixture containing nitrogen dioxide in nitrogen were compared to the response of the electron-capture detector which had been calibrated with pure nitrogen dioxide. A sample of the mixture of nitric oxide in nitrogen was oxidized by oxygen to nitrogen dioxide, and the concentration compared to the results for the mixture containing nitrogen dioxide in nitrogen.

An error of less than 0.5 percent was expected from the assumption of ideal gas behavior for nitrogen dioxide, nitric oxide and acetaldehyde at room temperature and one atmosphere pressure.

No pressure change less than 50 mm Hg was measured on the manometers with the cathetometer in the formation of the compositions of the initial reactants. The maximum errors in the initial concentrations of nitrogen dioxide, nitric oxide and acetaldehyde were less than two percent due to measurements of pressure.

The temperature fluctuations were less than $\pm$ 0.2°C during an oxidation test. The reduction of the total pressure in the reactor due to sampling was less than 3 mm Hg.

VI. RESULTS

A. Order of the Reaction

The order of the reaction between acetaldehyde and nitrogen dioxide was determined by measuring the initial rate of reaction of nitrogen dioxide at different initial concentrations of nitrogen dioxide and acetaldehyde. The initial conditions are summarized in Table 1. It was assumed that the initial rate of reaction of nitrogen dioxide could be expressed in the elementary form:

$$\left(\frac{d(NO_2)}{dt}\right)_{t=0} = - k \, (NO_2)^{\alpha}_{t=0} \, (CH_3CHO)^{\gamma}_{t=0} \qquad (66)$$

The initial concentration-time data for nitrogen dioxide from Tests 1 through 17 were fitted to equation (66). The order of the rate of disappearance of nitrogen dioxide with respect to acetaldehyde was found to be 1.00 $\pm$ 0.07 (0.07 is the 95 percent confidence limit for γ), and 1.00 $\pm$ 0.03 order with respect to nitrogen dioxide. The order of the reaction between acetaldehyde and nitrogen dioxide is illustrated in Figures 3 and 4.

At higher temperatures and pressures, previous investigators[9,20,40,47] also found that the reaction was

first-order with respect to acetaldehyde and nitrogen dioxide.

B. Initial Second-Order Rate Constant

The initial concentration-time data for nitrogen dioxide from Tests 1 through 17 were fitted to equation (66) with $\alpha = 1$ and $\gamma = 1$. The initial second-order rate constant for the disappearance of nitrogen dioxide was found to be $(8.596 \pm 0.189) \times 10^{-3}$ $l.mole^{-1}sec^{-1}$ at 22.0°C. The experimental rate of reaction of nitrogen dioxide is compared to the predicted rate of reaction in Table 2.

An initial second-order rate constant at 22.0°C was determined by Browning[9] of 1.0×10^{-3} $l.mole^{-1}sec^{-1}$, by Christie[20] of 7.45×10^{-4} $l.mole^{-1}sec^{-1}$, by McDowell and Thomas[40] of 1.0×10^{-2} $l.mole^{-1}sec^{-1}$, and by Pedlar and Pollard[47] of 1.06×10^{-3} $l.mole^{-1}sec^{-1}$. Only Christie actually obtained a rate constant at room temperature. All other investigators determined an expression for the rate constant based on data above 100°C. The rate constants at room temperature were calculated from these expressions.

C. Activation Energy

The activation energy of the reaction between acetaldehyde and nitrogen dioxide was evaluated from the tem-

perature dependence of the initial second-order rate constant and the Arrhenius equation:

$$k = k_o \exp(-E_A/RT) \qquad (67)$$

An activation energy of 12,900 ± 600 cal/mole was obtained in the temperature range of 22.0 to 122.3°C. The variation of the initial second-order rate constant with temperature is summarized in Table 3. Figure 5 is an Arrhenius plot for the rate of reaction of nitrogen dioxide.

In the literature, activation energies of 12,600 cal/mole[20], 13,500 cal/mole[9], 15,200 cal/mole[47] and 16,000 cal/mole[40] were reported for the reaction between nitrogen dioxide and acetaldehyde.

D. Products of the Reaction

Nitric oxide, carbon dioxide. methyl nitrite and nitromethane were the primary products of the partial oxidation of acetaldehyde by ppm concentrations of nitrogen dioxide at room temperature and atmospheric pressure. No methyl nitrate was observed, and only a trace amount of trans-dimeric nitrosomethane was identified.

The concentration-time data for nitrogen dioxide, nitric oxide, carbon dioxide, methyl nitrite and nitromethane are presented in Appendix A. The initial concen-

trations of acetaldehyde and nitrogen dioxide were varied in Tests 1 through 17. The concentration profiles for the reactants and products are illustrated for four tests in Figures 6, 7, 8 and 9.

The third-body effects due to the reduction of the total pressure of the reactor below one atmosphere were considered in Tests 18, 19 and 20. The rate of reaction and the formation of products were not affected by the reduction of the total pressure of the reactor from 760 to 400 mm Hg. The concentration-time data for the reactants and products are plotted for two tests in Figures 10 and 11.

Nitric oxide was introduced as an initial reactant, in addition to acetaldehyde and nitrogen dioxide, in Tests 21 through 25. The concentration profiles for the reactants and products are shown for three tests in Figures 12, 13 and 14.

Glass beads with a diameter of three millimeters were added to the reactor in Tests 26, 27 and 28. In Tests 29 and 30, glass wool was added to the reactor. There were no measurable surface effects on the reaction between nitrogen dioxide and acetaldehyde. The concentration-time data for the reactants and products are plotted for one test in Figure 15.

Figure 16 compares the concentrations of nitrogen dioxide as functions of time for Tests 2, 7 and 13. Figure 17 plots the concentrations of carbon dioxide as functions of time for Tests 1, 20 and 29. The concentration-time data for methyl nitrite for Tests 10, 28 and 30 are plotted in Figure 18. Figure 19 compares the concentration-time data for nitromethane for Tests 3, 8 and 15.

In Tests 1 through 20 and 26 through 30, the ratio of the concentration of nitric oxide to the concentration of carbon dioxide was constant throughout the reactions. The ratio of nitric oxide to carbon dioxide was 1.5.

The ratio of the concentration of methyl nitrite to the concentration of nitromethane was not constant throughout a reaction. The ratio of methyl nitrite to nitromethane decreased as the reaction proceeded.

In all tests, the sum of the concentrations of methyl nitrite and nitromethane was equal to the concentration of carbon dioxide throughout the reaction.

In Tests 21 through 25, the addition of initial nitric oxide to the normal reactants, acetaldehyde and nitrogen dioxide, did not affect the rate of disappearance of nitrogen dioxide or the rate of formation of carbon dioxide. The addition of initial nitric oxide increased the rate of formation of nitromethane and decreased the rate of for-

mation of methyl nitrite. Figures 20 and 21 compare the experimental concentrations of nitromethane and methyl nitrite with the concentrations predicted for no initial nitric oxide for Tests 23 and 25.

There was no measurable reaction between nitric oxide and acetaldehyde at room temperature.

E. Reaction Mechanism

The reaction scheme was required to satisfy the following experimental results:

(1) The initial rate of disappearance of nitrogen dioxide was first-order in acetaldehyde and nitrogen dioxide.

(2) The initial second-order rate constant for the disappearance of nitrogen dioxide was 8.596×10^{-3} l. $mole^{-1} sec^{-1}$.

(3) The ratio of the concentration of nitric oxide to the concentration of carbon dioxide was 1.5 throughout the reaction.

(4) The sum of the concentrations of methyl nitrite and nitromethane was equal to the concentration of carbon dioxide during a reaction.

(5) The ratio of the concentration of methyl nitrite to the concentration of nitromethane was not constant during a reaction, but decreased as the reaction proceeded.

(6) The rate of consumption of nitrogen dioxide and the rate of formation of carbon dioxide were not affected by the concentration of nitric oxide.

(7) Increased concentration of nitric oxide increased the rate of formation of nitromethane and decreased the rate of formation of methyl nitrite.

(8) No methyl nitrate was formed by the acetaldehyde-nitrogen dioxide reaction.

With these requirements, the following reaction scheme is proposed:

$$CH_3CHO + NO_2 \xrightarrow{k_1} CH_3CO + HNO_2 \quad (68)$$

$$CH_3CO + NO_2 \xrightarrow{k_2} CH_3 + CO_2 + NO \quad (69)$$

$$CH_3 + NO_2 \xrightarrow{k_3} CH_3NO_2 \quad (70)$$

$$CH_3 + NO_2 \xrightarrow{k_4} CH_3ONO \quad (71)$$

$$CH_3 + NO \xrightarrow{k_5} CH_3NO \quad (72)$$

$$CH_3NO + NO_2 \xrightarrow{k_6} CH_3NO_2 + NO \quad (73)$$

$$2\ CH_3NO \underset{k'_7}{\overset{k_7}{\rightleftharpoons}} (CH_3NO)_2 \quad (74)$$

$$2\ HNO_2 \underset{k'_8}{\overset{k_8}{\rightleftharpoons}} H_2O + NO + NO_2 \quad (75)$$

$$CH_3NO + 2\ NO \xrightarrow{k_9} CH_3 + N_2 + NO_3 \quad (76)$$

$$NO_3 + NO \xrightarrow{k_{10}} 2\ NO_2 \quad (77)$$

In the development of the rate expressions, the following assumptions were made concerning the reaction scheme:

(1) Reactions (74), (76) and (77) were negligible.

(2) Reaction (75) was very rapid, and the equilibrium was far to the right.

(3) The concentrations of the radicals, CH_3 and CH_3CO, and the concentration of the intermediates, HNO_2 and CH_3NO, were small compared to the concentrations of reactants and products. A steady-state assumption was made for each of these components.

With these assumptions, the following rate expressions were obtained for nitrogen dioxide, nitric oxide, carbon dioxide, methyl nitrite and nitromethane:

$$r_{NO_2} = -2.5\, k_1\, (CH_3CHO)(NO_2) \tag{78}$$

$$r_{NO} = 1.5\, k_1\, (CH_3CHO)(NO_2) \tag{79}$$

$$r_{CO_2} = k_1\, (CH_3CHO)(NO_2) \tag{80}$$

$$r_{CH_3ONO} = \frac{k_1 k_4\, (CH_3CHO)(NO_2)^2}{(k_3+k_4)(NO_2) + k_5(NO)} \tag{81}$$

$$r_{CH_3NO_2} = \frac{k_1(CH_3CHO)(NO_2)\left[k_3(NO_2) + k_5(NO)\right]}{(k_3+k_4)(NO_2) + k_5(NO)} \tag{82}$$

The rate expressions for nitrogen dioxide nitric oxide, carbon dioxide, methyl nitrite and nitromethane were integrated with the initial conditions:

A = initial concentration of acetaldehyde

$(NO_2)_o$ = initial concentration of nitrogen dioxide

$(NO)_o$ = initial concentration of nitric oxide

The following expressions for the concentrations as functions of time were obtained:

$$(NO_2) = (NO_2)_o \exp(-2.5k_1At) \quad (83)$$

$$(NO) = (NO)_o + 0.6\,(NO_2)_o \left[1 - \exp(-2.5k_1At)\right] \quad (84)$$

$$(CO_2) = 0.4\,(NO_2)_o \left[1 - \exp(-2.5k_1At)\right] \quad (85)$$

$$(CH_3ONO) = a + b \ln (c) \quad (86)$$

$$(CH_3NO_2) = d + e \ln (c) \quad (87)$$

where

$$a = \frac{.4k_4(NO_2)_o}{k_3+k_4-.6k_8} \left\{1 - \exp(-2.5k_1At)\right\} \quad (89)$$

$$b = \frac{.4k_4k_5}{(k_3+k_4-.6k_5)^2} \left\{(NO)_o + .6(NO_2)_o\right\} \quad (90)$$

$$c = \frac{k_5 (NO)_o + .6(NO_2)_o}{(k_3+k_4)(NO_2)_o + k_5(NO)_o} + \tag{91}$$

$$\frac{(k_3+k_4-.6k_5)(NO_2)_o}{(k_3+k_4)(NO_2)_o + k_5(NO)_o} \exp(-2.5k_1At) \tag{92}$$

$$d = \frac{.4(k_3-.6k_5)(NO_2)_o}{k_3+k_4-.6k_5} \left\{1 - \exp(-2.5k_1At)\right\} \tag{93}$$

$$e = \frac{.4k_5 (NO)_o + .6(NO_2)_o}{k_3+k_4-.6k_5} \left\{ \frac{k_4-.6k_5}{k_3+k_4-.6k_5} - 1 \right\} \tag{94}$$

The data for the concentration of nitrogen dioxide as a function of time were used to evaluate k_1 from equation (83). The value of $2.5k_1$ was found to be $(8.596 \pm 0.189) \times 10^{-3}$ $l.mole^{-1}sec^{-1}$ at 22.0^oC.

The data for the initial rates of formation of methyl nitrite and nitromethane were used to evaluate the ratio of the rate constants k_4/k_3. At the beginning of the reaction between acetaldehyde and nitrogen dioxide, the concentration of nitric oxide was small. A ratio of the initial rates of formation of methyl nitrite and nitromethane was obtained by dividing equation (81) by equation (82), with (NO) = 0:

$$\frac{\left(\frac{d(CH_3ONO)}{dt}\right)_{t=0}}{\left(\frac{d(CH_3NO_2)}{dt}\right)_{t=0}} = \frac{k_4}{k_3} \qquad (95)$$

Based on the ratio of the initial rates of formation of methyl nitrite and nitromethane, k_4/k_3 was found to be 2.17.

The ratio of the rate constants k_5/k_3 was evaluated from equation (81), the rate expression for methyl nitrite. Rearrangement of equation (81) yielded:

$$\frac{k_5}{k_3} = \frac{k_1 k_4 (CH_3CHO)(NO_2)^2}{k_3(NO)\left(\frac{d(CH_3CONO)}{dt}\right)} - \frac{(NO_2)^2}{(NO)}\left\{1 - \frac{k_4}{k_3}\right\} \qquad (96)$$

The ratio of the rate constants, k_5/k_3, was evaluated using the concentrations of nitrogen dioxide, nitric oxide and acetaldehyde as functions of time, and the values previously determined for k_1 and k_4/k_3. The value of k_5/k_3 was found to be 0.62.

The reaction mechanism, with the three assumptions previously noted, allowed the best prediction of the experimentally determined concentration-time profiles for

nitrogen dioxide, nitric oxide, carbon dioxide, methyl nitrite and nitromethane. In Figures 6 through 24, the experimental concentrations are compared to the concentrations predicted by equation (83) for nitrogen dioxide, by equation (84) for nitric oxide, by equation (85) for carbon dioxide, by equation (86) for methyl nitrite, and by equation (87) for nitromethane. Figures 20 and 21 illustrate the comparison between (1)the experimental concentrations of methyl nitrite and nitromethane, (2)the predicted concentrations, and (3)the concentrations predicted if the tests had no initial nitric oxide. Figures 22 and 23 show the difference between (1)the experimental concentrations of methyl nitrite and nitromethane, (2)the predicted concentrations, and (3)the concentrations predicted for methyl nitrite and nitromethane if the methyl radicals only reacted with nitrogen dioxide. Figure 24, for Test 22, compares (1)the experimental concentrations of methyl nitrite and nitromethane, (2)the predicted concentrations, (3)the predicted concentrations for no initial nitric oxide, and (4)the predicted concentrations for no nitric oxide reacting with methyl radicals.

VII. DISCUSSION

A. Reaction Mechanism

The rate-determining reaction in the acetaldehyde-nitrogen dioxide scheme was the initial reaction between acetaldehyde and nitrogen dioxide to produce an acetyl radical and nitrous acid:

$$CH_3CHO + NO_2 \longrightarrow CH_3CO + HNO_2 \qquad (97)$$

The reaction was first proposed by McDowell and Thomas[40] and incorporated into the mechanisms of subsequent investigators[9,47,49,59]. This reaction was very much slower than the other reactions in the mechanism because it was the only reaction between two stable molecules. All the other reactions in the scheme were between radicals and molecules or between unstable intermediates and molecules.

The acetyl radical reacted with nitrogen dioxide via the acetyloxy intermediate[40,52] or the acetyl nitrite intermediate[47] to form a methyl radical, carbon dioxide and nitric oxide:

$$CH_3CO + NO_2 \longrightarrow CH_3 + CO_2 + NO \qquad (98)$$

In reaction (98), one mole of carbon dioxide is produced for each mole of methyl radicals. If this is the only reaction producing carbon dioxide and methyl radicals, the concentration of carbon dioxide is a measure of the moles of methyl radicals produced. In this experiment, the concentration of carbon dioxide was equal to the sum of the concentrations of methyl nitrite and nitromethane. Therefore, methyl nitrite and nitromethane were the principal organic products of the reaction between acetaldehyde and nitrogen dioxide at room temperature.

Christie and Voisey[19] found that the acetyl radical-nitrogen dioxide reaction proceeded five times faster than the corresponding acetyl radical-nitric oxide reaction at room temperature. The reaction between the acetyl radical and nitric oxide was postulated to be the first step in the disproportionation of nitric oxide by acetyl radicals[16, 19]:

$$CH_3CO + NO \longrightarrow CH_3CONO \qquad (99)$$

$$CH_3CONO + 2\ NO \longrightarrow CH_3CO + N_2 + NO_3 \qquad (100)$$

$$NO_3 + NO \longrightarrow 2\ NO_2 \qquad (101)$$

The disproportionation of nitric oxide was not included

in the reaction mechanism. Reactions (99), (100) and (101) would only be significant when the concentration of nitric oxide was very much greater than the concentration of nitrogen dioxide. The overall reaction for the disproportionation of nitric oxide to nitrogen dioxide and nitrogen was:

$$4\ NO \longrightarrow 2\ NO_2 + N_2 \qquad (102)$$

The concentration of nitrogen would be a measure of the moles of nitrogen dioxide produced by the disproportionatiom of nitric oxide. Phillips and Shaw[49] reported that very little nitrogen was produced by the reaction between acetaldehyde and nitrogen dioxide. The concentration of nitrogen was not monitored in this experiment.

Nitromethane was one of the products formed by the direct combination of methyl radicals and nitrogen dioxide:

$$CH_3 + NO \longrightarrow CH_3NO_2 \qquad (103)$$

The results of this investigation showed that reaction (103) was the principal source of nitromethane at room temperature. Gray[27] postulated that reaction (103) was very probable at room temperature. Patsevich, Topchiev

and Shtern[46] experimentally observed that reaction (103) was the predominant reaction between methyl radicals and nitrogen dioxide at room temperature and low pressures. Rebbert and Slagg[51] also experimentally identified reaction (103), but found it was not the predominant reaction between methyl radicals and nitrogen dioxide.

Phillips snd Shaw[49] suggested the formation of nitromethane from the reaction between nitrosomethane and nitrogen dioxide:

$$CH_3NO + NO_2 \longrightarrow CH_3NO_2 + NO \qquad (104)$$

In this experiment, the concentration of nitromethane as a function of time showed that reaction (104) contributed to the production of nitromethane. As the reaction between acetaldehyde and nitrogen dioxide proceeded, the concentration of nitrogen dioxide decreased and the concentration of nitric oxide increased. Nitric oxide and nitrogen dioxide competed for the methyl radicals. Experimentally, nitrogen dioxide reacted with methyl radicals to form methyl nitrite and nitromethane in the ratio of 2.17:1. The ratio of the concentration of methyl nitrite to the concentration of nitromethane would have remained constant at a value of 2.17 if no nitric oxide were present (Fig-

ures 22, 23 and 24). It was experimentally determined that the ratio of the concentrations of methyl nitrite to nitromethane decreased as the reaction between acetaldehyde and nitrogen dioxide proceeded. This was due to the reaction between nitric oxide and methyl radicals to form nitrosomethane. The nitrosomethane reacted with nitrogen dioxide to form nitromethane and regenerate nitric oxide by reaction (104). Therefore, nitric oxide increased the rate of formation of nitromethane and decreased the rate of formation of methyl nitrite.

Methyl nitrite was the second product formed by the direct combination of methyl radicals and nitrogen dioxide.

$$CH_3 + NO_2 \longrightarrow CH_3ONO \qquad (105)$$

The results of this investigation showed that reaction (105) was the only source of methyl nitrite at room temperature and atmospheric pressure. The experimental results indicated that the rate of formation of methyl nitrite was greater than the rate of formation of nitromethane, $k_{105}/k_{103} = 2.17$. Patsevich, Topchiev and Shtern[46] experimentally identified reaction (105) at room temperature and reduced pressure, but found the rate of formation

of nitromethane was greater than the rate of formation of methyl nitrite, $k_{105}/k_{103} = 0.33$. Rebbert and Slagg[51] also observed reaction (105) at room temperature and reduced pressure. They also found that the rate of formation of nitromethane was greater than the rate of formation of methyl nitrite, $k_{105}/k_{103} = 0.13$, but concluded that the ratio of the rate constants was pressure dependent.

One explanation for the disagreement between the results of this experiment and the conclusions of Patsevich, Topchiev and Shtern[46] and Rebbert and Slagg[51], could be the total pressure of the reactions investigated. The previous investigators studied the reactions at total pressures below 3 mm Hg, whereas this study was performed at total pressures near 760 mm Hg. At low pressures, reaction (105) was probably third-body dependent[27], and nitromethane was formed faster than methyl nitrite. At higher pressures, reaction (105) followed second-order kinetics, and methyl nitrite was formed faster than nitromethane. Tests 18, 19 and 20 showed no effect on the rate of reaction or distribution of products with a reduction of the total pressure of the reactor from 760 to 400 mm Hg. This indicated reaction (105) was second-order above 400 mm Hg. The pressure range for the transition from

third-order kinetics to second order kinetics is probably between 100 and 200 mm Hg[14,30,54].

As the reaction between acetaldehyde and nitrogen dioxide proceeded, the concentration of nitric oxide increased. The nitric oxide reacted with methyl radicals to form nitrosomethane:

$$CH_3 + NO \longrightarrow CH_3NO \qquad (106)$$

In the literature, the second-order rate constant varied between 10^6 and 10^9 $l.mole^{-1}sec^{-1}$ at room temperature[14,42,54]. The reaction was reported to be second-order above a pressure of 200 mm Hg[14,30,49,54]. The nitrosomethane formed by reaction (106), reacted with nitrogen dioxide to form nitromethane and nitric oxide by reaction (104). In this experiment, the nitrosomethane intermediate was not experimentally identified.

In this study, a white crystalline solid with a melting point of 119-121°C was a product of the reaction between acetaldehyde (100 mm Hg) and nitrogen dioxide (10 mm Hg) at room temperature and a total pressure of one atmosphere. No solid was observed for the partial oxidation of acetaldehyde by ppm concentrations of nitrogen dioxide. The crystals were concluded to be a stable dimer

of nitrosomethane[13,26]:

$$2\ CH_3NO \rightleftharpoons (CH_3NO)_2 \qquad (107)$$

Various investigators[12,15,17,31] obtained values between 12 and 87 $l.mole^{-1}sec^{-1}$ for the second-order rate constant for the dimerization of nitrosomethane at 25°C. The rates of the thermal decomposition of the dimers of nitrosomethane were also measured[5,17]. In the reaction mechanism, reaction (107) was assumed to be negligible since no measurable amount of dimeric nitrosomethane was identified for the reaction between ppm concentrations of nitrogen dioxide and excess acetaldehyde. This assumption was also made since the rate constant for the dimerization of nitrosomethane, 12 to 87 $l.mole^{-1}sec^{-1}$, was significantly less than the rate constants for the other second-order reactions, 10^6 to 10^9 $l.mole^{-1}sec^{-1}$.

At the later stages of the reaction between nitrogen dioxide and acetaldehyde, the concentration of nitric oxide was much greater than the concentration of nitrogen dioxide. Therefore, the nitrosomethane reacted with nitric oxide:

$$CH_3NO + 2\ NO \longrightarrow CH_3 + NO_3 + N_2 \qquad (108)$$

$$NO_3 + NO \longrightarrow 2\ NO_2 \qquad (109)$$

Christie, et. al.[15,17,18], concluded that this sequence was the reaction scheme for the disproportionation of nitric oxide to nitrogen dioxide and nitrogen via the methyl radical. They found that the rate-determining step for the disproportionation of nitric oxide was first-order in nitrosomethane and second-order in nitric oxide. The third-order rate constant was determined to be 55 $l.mole^{-1}$ sec^{-1} by Christie[15], and 47 $l.mole^{-1}sec^{-1}$ by Johnston and Heicklen[31]. Christie and Voisey[19] reported that the reaction between acetyl radicals and nitrogen dioxide was five times faster than the reaction between acetyl radicals and nitric oxide. They also found that the disproportionation of nitric oxide by acetyl radicals was twenty times faster than the disproportionation of nitric oxide by methyl radicals. In the derivation of the rate expressions for the reaction between acetaldehyde and nitrogen dioxide, reactions (108) and (109) were assumed to be negligible. This assumption was made because the reaction between acetyl radicals and nitrogen dioxide was at least one humdred times faster than the disproportionation of nitric oxide by methyl radicals.

Nitrous acid was not identified in this study. It was assumed that nitrous acid instantaneously formed water, nitric oxide and nitrogen dioxide[41,64]:

$$2\ HNO_2 \rightleftharpoons H_2O + NO + NO_2 \quad (110)$$

B. Auxiliary Reactions

Methyl nitrate was not a product of the reaction between acetaldehyde and nitrogen dioxide at room temperature and a total pressure of one atmosphere. Therefore, the reaction between methyl radicals and nitrogen dioxide to form methoxy radicals and nitric oxide did not occur:

$$CH_3 + NO_2 \longrightarrow CH_3O + NO \qquad (111)$$

Patsevich, Topchiev and Shtern[46] substantiate the results of this investigation, as they found no evidence for reaction (111) at room temperature and reduced pressures. In contrast, Gray[27] postulated that reaction (111) was the predominant reaction between methyl radicals and nitrogen dioxide. He stated that any methyl nitrite formed from the direct combination of methyl radicals and nitrogen dioxide would instantaneously decompose, with reaction (111) as the over-all scheme.

In the literature, reaction (111) was significant above 50°C. Browning[9] and Phillips and Shaw[49] identified methyl nitrate as a product of the reaction between acetaldehyde and nitrogen dioxide above 50°C:

$$CH_3O + NO_2 \longrightarrow CH_3ONO_2 \qquad (112)$$

Rebbert and Slagg[51] and Johnston and Heicklen[31] identified methyl nitrate as a product of the reaction between methyl radicals and nitrogen dioxide. Allen and Bagley[1] and Avery and Cvetanovic[3] reported that methyl nitrate was a secondary product of the photochemical reaction between acetaldehyde and nitrogen dioxide at room temperature.

When methoxy radicals were produced by reaction (111), methyl nitrite was formed by the combination of methoxy radicals with nitric oxide:

$$CH_3O + NO \longrightarrow CH_3ONO \qquad (113)$$

Previous investigators[1,3,9,27,31,49] concluded that reaction (113) was the only source of methyl nitrite at their experimental conditions. The results of this experiment showed that methoxy radicals were not produced, methyl nitrate was not formed, and methyl nitrite was not produced by reaction (113) at room temperature and a total pressure of one atmosphere. Reaction (105), the direct combination of methyl radicals and nitrogen dioxide, was the only source of methyl nitrite.

The isomerization and subsequent decomposition of nitrosomethane at temperatures above 200°C have been re-

ported[4,11,50,58]:

$$CH_3 + NO \longrightarrow CH_3NO \quad (114)$$

$$CH_3NO \longrightarrow CH_2NOH \quad (115)$$

$$CH_2NOH \longrightarrow HCONH_2 \quad (116)$$

$$CH_2NOH \longrightarrow HCN + H_2O \quad (117)$$

$$HCONH_2 \longrightarrow NH_3 + CO \quad (118)$$

The isomerization of nitrosomethane was insignificant in this experiment because formaldoxime and formamide were not reaction products. Hydrogen cyanide, ammonia and carbon monoxide were not produced by the reaction between acetaldehyde and nitrogen dioxide at room temperature.

Trimethylhydroxylamine was the product of the reaction between nitrosomethane and excess methyl radicals[7, 30,37,48]:

$$CH_3NO + 2\ CH_3 \longrightarrow (CH_3)_2NOCH_3 \quad (119)$$

The results of this experiment showed that all methyl radicals were consumed by nitrogen dioxide and nitric oxide, and no trimethylhydroxylamine was produced.

Johnston and Heicklen[31] reported a first-order reac-

tion with respect to nitric oxide and nitrosomethane at 25°C. Nitrous oxide was produced by this photochemical reaction:

$$CH_3NO + NO \longrightarrow N_2O + CH_3O \qquad (120)$$

Reaction (120) was negligible in the acetaldehyde-nitrogen dioxide system because nitrous oxide was not a product of the reaction.

Allen and Bagley[1] identified methyl acetate and nitrous oxide as products of the room temperature photolysis of acetaldehyde and nitrogen dioxide:

$$CH_3NO + CH_3ONO \longrightarrow CH_3CO_2CH_3 + N_2O \qquad (121)$$

In this experiment, reaction (121) did not occur since neither methyl acetate nor nitrous oxide were identified as products of the reaction.

McDowell and Thomas[40] postulated the formation of acetic acid from the reaction between acetaldehyde and nitrogen dioxide:

$$CH_3CO_2 + HNO_2 \longrightarrow CH_3CO_2H + NO_2 \qquad (122)$$

The results of this study showed that acetic acid was not a product of the reaction.

Methane and carbon monoxide were the primary products of the pyrolysis of acetaldehyde at high temperatures[33, 34,35,62,63,65]. Very small quantities of ethane and hydrogen were also identified as secondary products of the pyrolysis:

$$CH_3CHO \longrightarrow CH_4 + CO \qquad (123)$$

$$2\ CH_4 \longrightarrow C_2H_6 + H_2 \qquad (124)$$

Since no methane or ethane were formed by the reaction between acetaldehyde and nitrogen dioxide, reactions (123) and (124) were negligible at room temperature.

Reactions between methyl and acetyl radicals were considered, but these reactions were negligible since ethane, acetone and biacetyl were not products of the reaction between acetaldehyde and nitrogen dioxide:

$$CH_3 + CH_3 \longrightarrow CH_3CH_3 \qquad (125)$$

$$CH_3CO + CH_3 \longrightarrow (CH_3)_2CO \qquad (126)$$

$$CH_3CO + CH_3CO \longrightarrow (CH_3CO)_2 \qquad (127)$$

C. Summary

The primary products of the reaction between acetaldehyde and nitrogen dioxide were nitric oxide, carbon dioxide, methyl nitrite and nitromethane. A trace amount of trans-dimeric nitrosomethane was also identified as a product of the reaction. No methyl nitrate was produced, therefore methoxy radicals were not formed. Since methoxy radicals were not formed, methyl nitrite was only produced by the direct combination of methyl radicals and nitrogen dioxide. Nitrosomethane did not isomerize because formaldoxime and formamide were not observed. Organic radicals did not recombine since ethane, acetone and biacetyl were not products of the reaction. Nitrous oxide was not isolated as a product of the reaction.

In the reaction between acetaldehyde and nitrogen dioxide at room temperature and a total pressure of one atmosphere, 0.6 moles of nitric oxide and 0.4 moles of carbon dioxide were formed for each mole of nitrogen dioxide consumed. For each mole of carbon dioxide produced, one mole of methyl radicals was created. Initially, the rate of formation of methyl nitrite was greater than the rate of formation of nitromethane. The concentration of nitric oxide increased as the reaction proceeded, and the nitric oxide reacted with methyl radicals to form nitroso-

methane. The nitrosomethane reacted with nitrogen dioxide to form nitromethane and regenerate nitric oxide. Therefore, as the concentration of nitric oxide increased, the rate of formation of nitromethane increased and the rate of formation of methyl nitrite decreased. In the final stages of the reaction, the concentration of nitric oxide was much greater than the concentration of nitrogen dioxide, and the disproportionation of nitric oxide to form nitrogen dioxide and nitrogen occurred to some extent. The disproportionation sequence was the principal mechanism responsible for the deviation from second-order kinetics in the final stages of the acetaldehyde-nitrogen dioxide reaction.

VIII. CONCLUSIONS

The following conclusions can be drawn about the partial oxidation of acetaldehyde by ppm concentrations of nitrogen dioxide at 22.0°C and a total pressure of one atmosphere:

The rate of disappearance of nitrogen dioxide is 1.00 ± 0.07 order with respect to acetaldehyde and 1.00 ± 0.03 order with respect to nitrogen dioxide.

The initial second-order rate constant for the disappearance of nitrogen dioxide is $(8.596 \pm 0.189) \times 10^{-3}$ l. $mole^{-1} sec^{-1}$ at 22.0°C.

The activation energy for the reaction between acetaldehyde and nitrogen dioxide is 12,900 cal/mole in the temperature range between 22 and 122°C.

There are no measurable surface effects due to the addition of glass beads or glass wool to the reactor.

The products of the reaction are nitric oxide, carbon dioxide, methyl nitrite, nitromethane and a trace amount of trans-dimeric nitrosomethane.

A mechanism incorporating the major features of the reaction between acetaldehyde and nitrogen dioxide is proposed:

$$CH_3CHO + NO_2 \longrightarrow CH_3CO + HNO_2 \quad (1)$$

$$CH_3CO + NO_2 \longrightarrow CH_3 + CO_2 + NO \quad (2)$$

$$CH_3 + NO_2 \longrightarrow CH_3NO_2 \quad (3)$$

$$CH_3 + NO_2 \longrightarrow CH_3ONO \quad (4)$$

$$CH_3 + NO \longrightarrow CH_3NO \quad (5)$$

$$CH_3NO + NO_2 \longrightarrow CH_3NO_2 + NO \quad (6)$$

$$2\ CH_3NO \rightleftharpoons (CH_3NO)_2 \quad (7)$$

$$2\ HNO_2 \rightleftharpoons H_2O + NO + NO_2 \quad (8)$$

$$CH_3NO + 2\ NO \longrightarrow CH_3 + N_2 + NO_3 \quad (9)$$

$$NO_3 + NO \longrightarrow 2\ NO_2 \quad (10)$$

Assuming that reactions (7), (9) and (10) are negligible, reaction (8) is very fast and the equilibrium is far to the right, and making a steady-state assumption for CH_3CO, CH_3, CH_3NO and HNO_2, the following expressions for the concentrations of products of the reaction as functions of time are obtained:

$$(NO_2) = (NO_2)_o \exp(-2.5k_1At)$$

$$(NO) = (NO)_o + 0.6\ (NO_2)_o \left[1 - \exp(-2.5k_1At)\right]$$

$$(CO_2) = 0.4\ (NO_2)_o \left[1 - \exp(-2.5k_1At)\right]$$

$(CH_3ONO) = a + b \ln (c)$

$(CH_3NO_2) = d + e \ln (c)$

Where

$(NO_2)_o$ = initial concentration of nitrogen dioxide

$(NO)_o$ = initial concentration of nitric oxide

k_1 = second-order rate constant for reaction (1)

A = initial concentration of acetaldehyde

t = time

$$a = \frac{.4k_4(NO_2)_o}{k_3+k_4-.6k_8} \left\{ 1 - \exp(-2.5k_1At) \right\}$$

$$b = \frac{.4k_4k_5}{(k_3+k_4-.6k_5)^2} \left\{ (NO)_o + .6(NO_2)_o \right\}$$

$$c = \frac{k_5(NO)_o + .6(NO_2)_o}{(k_3+k_4)(NO_2)_o + k_5(NO)_o} + \frac{(k_3+k_4-.6k_5)(NO_2)_o}{(k_3+k_4)(NO_2)_o + k_5(NO)_o} \exp(-2.5k_1At)$$

$$d = \frac{.4(k_3-.6k_5)(NO_2)_o}{k_3+k_4-.6k_5} \left\{ 1 - \exp(-2.5k_1At) \right\}$$

$$e = \frac{.4k_5 (NO)_o + .6(NO_2)_o}{k_3+k_4-.6k_5} \left\{ \frac{k_4-.6k_5}{k_3+k_4-.6k_5} - 1 \right\}$$

The value of $2.5k_1$ is 8.596×10^{-3} $1.mole^{-1}sec^{-1}$ at $22.0^{o}C$. The ratio of the rate constants k_4/k_3 is 2.17, and k_5/k_3 is 0.62.

The study is unique because there has been no previous investigation of (1)the reaction between acetaldehyde and nitrogen dioxide at room temperature, (2)the reactions between organic radicals and the oxides of nitrogen at pressures near one atmosphere, and (3)the concentrations of the reactants and products of the reactions as functions of time. Previous investigators only used the concentration of nitrogen dioxide as a function of time and the quantitative analysis of the final products of the reactions. The concentration-time data for reactants and products allow the formulation of a reaction mechanism, the evaluation of relative rate constants, and the prediction of concentrations of reactants and products as functions of time for the reaction between acetaldehyde and nitrogen dioxide.

The results of the study are also unique because no methoxy radicals were produced below $40^{o}C$ by the reaction between acetaldehyde and nitrogen dioxide. All methyl nitrite produced in the reaction between acetaldehyde and nitrogen dioxide was formed by the direct combination of methyl radicals and nitrogen dioxide. Since no methoxy radicals were produced and no methyl nitrate was formed, an orginal reaction mechanism is postulated.

IX. RECOMMENDATIONS

It would be of interest to investigate the reaction between acetaldehyde and nitrogen dioxide at room temperature and pressures below one atmosphere. A study of this type would yield information concerning the pressure range for the transition from third-order kinetics to second-order kinetics for the reactions between methyl radicals and nitric oxide and nitrogen dioxide.

Investigation of the reaction between nitrogen dioxide and acetaldehyde in the temperature range between 20 and 180°C would produce significant information about the formation of methoxy radicals. At room temperature no methoxy radicals are produced, and methyl nitrite is formed from the direct combination of methyl radicals and nitrogen dioxide. In contrast, above 100°C the direct reaction between methyl radicals and nitrogen dioxide produces methoxy radicals and nitric oxide. Methyl nitrite is only formed from the reaction between methoxy radicals and nitric oxide. Therefore, in the temperature range between 20 and 180°C there are two reactions participating in the formation of methyl nitrite.

Experiments with high initial concentrations of nitric oxide in the acetaldehyde-nitrogen dioxide system would

yield information concerning the importance of the disproportionation of nitric oxide by methyl and acetyl radicals.

Any future work on the reaction between acetaldehyde and nitrogen dioxide would require quantitative analysis of nitric oxide and nitrogen. The determination of nitrogen could be accomplished by gas chromatography employing an argon-ionization detector.

Further studies on the reactions between the organic radicals and the oxides of nitrogen are necessary. Photochemical reactions could provide a source of methyl and methoxy radicals for combination with nitric oxide and nitrogen dioxide.

In order to understand the reactions which occur in the atmosphere, investigations of the thermal and photochemical reactions among the oxides of nitrogen, organic compounds, oxygen and water are necessary.

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XI. NOMENCLATURE

C	Concentration, moles/liter
E_A	Activation Energy, calories/mole
k_i	Rate Constant for Reaction (i), appropiate units
n_i	Moles of Component i
p_i	Partial Pressure of Component i, mm of mercury
ppm	Parts Per Million, v/v
R	Gas Constant, 1.987 $cal.mole^{-1}\ {}^{o}K^{-1}$
t	Time, minutes
T	Temperature, ${}^{o}K$
$()$	Concentration, moles/liter
$()_o$	Initial Concentration, moles/liter
$\left(\frac{d()}{dt}\right)_{t=0}$	Slope of the Concentration-Time Curve at t=0 moles/(liter)(minute)

NOMENCLATURE, continued

Compound	Formula
Acetaldehyde	CH_3CHO
Acetic Acid	CH_3CO_2H
Acetyl Nitrite	$CH_3CO(NO)$
Acetyl Radical	CH_3CO
Acetyloxy Radical	CH_3CO_2
Acetone	$(CH_3)_2CO$
Ammonia	NH_3
Biacetyl	(CH_3CO)
Carbon Dioxide	CO_2
Carbon Monoxide	CO
Dimeric Nitrosomethane	$(CH_3NO)_2$
Ethane	C_2H_6
Formaldoxime	CH_2NOH
Formamide	$HCONH_2$
Glyoxal	$(CHO)_2$
Hydrogen Cyanide	HCN
Methane	CH_4
Methyl Acetate	$CH_3CO_2CH_3$
Methyl Nitrate	CH_3ONO_2
Methyl Nitrite	CH_3ONO
Methyl Radical	CH_3

NOMENCLATURE, continued

Compound	Formula
Methoxy Radical	CH_3O
Nitric Oxide	NO
Nitrogen	N_2
Nitrogen Dioxide	NO_2
Nitrogen Trioxide	NO_3
Nitrosomethane	CH_3NO
Nitrous Acid	HNO_2
Nitrous Oxide	N_2O
N-methyl-N-nitrosohydroxylamine nitrite	$CH_3N(ONO)NO$
2-nitrosoethan-2-al	$CH_3CO(NO)$
Trimethylhydroxylamine	$(CH_3)_2NOCH_3$

LIST OF TABLES

Table 1. Initial Conditions for the Partial Oxidation of Acetaldehyde.

Test	Temp.	Press.	Nitrogen Dioxide Press.	Nitrogen Dioxide Conc.	Acetaldehyde Press.	Acetaldehyde Conc.	Nitric Oxide Press.	Nitric Oxide Conc.
	°C	mm Hg	10^{-3} mm Hg	10^{-7} mol/l	mm Hg	10^{-3} mol/l	10^{-5} mm Hg	10^{-7} mol/l
1	22.1	754.7	15.63	8.49	74.4	4.04	0.	0.
2	22.0	757.2	15.11	8.21	48.4	2.65	0.	0.
3	22.3	768.4	22.95	12.47	126.6	6.88	0.	0.
4	21.9	760.9	18.00	9.78	123.3	6.70	0.	0.
5	22.4	765.6	19.71	10.71	35.5	1.93	0.	0.
6	22.0	755.5	14.74	8.01	146.9	7.98	0.	0.
7	21.7	775.1	18.56	10.08	22.8	1.24	0.	0.
8	22.0	759.0	12.46	6.77	51.6	2.80	0.	0.
9	22.0	771.8	12.19	6.62	130.0	7.06	0.	0.
10	22.0	752.8	12.85	6.98	146.7	7.97	0.	0.
11	22.0	772.2	15.54	8.44	77.1	4.19	0.	0.
12	21.8	768.1	11.65	6.33	80.3	4.36	0.	0.
13	21.9	753.6	13.82	7.51	86.6	4.70	0.	0.
14	22.0	760.8	17.32	9.41	56.9	3.09	0.	0.
15	22.6	757.8	14.36	7.80	104.6	5.68	0.	0.
16	22.3	762.7	12.72	6.91	108.9	5.92	0.	0.
17	21.9	768.6	23.58	12.81	120.8	6.56	0.	0.
18	22.0	608.7	21.96	11.93	69.2	3.76	0.	0.
19	22.0	516.6	11.97	6.50	67.4	3.66	0.	0.
20	22.3	407.3	21.92	11.91	92.2	5.01	0.	0.

Table 1, continued

Test	Temp.	Press.	Nitrogen Dioxide Press.	Nitrogen Dioxide Conc.	Acetaldehyde Press.	Acetaldehyde Conc.	Nitric Oxide Press.	Nitric Oxide Conc.
	°C	mm Hg	10^{-3} mm Hg	10^{-7} mol/l	mm Hg	10^{-3} mol/l	10^{-4} mm Hg	10^{-7} mol/l
21	22.2	764.2	16.92	9.19	95.3	5.18	6.97	0.38
22	22.1	773.4	14.39	7.82	101.3	5.50	11.96	0.65
23	22.0	757.2	18.21	9.89	87.7	4.76	23.38	1.27
24	22.5	768.7	15.40	8.37	114.2	6.20	24.90	1.35
25	21.9	758.6	17.87	9.71	78.6	4.27	36.83	2.00
26	22.0	761.2	13.25	7.20	85.4	4.64	0.	0.
27	22.3	749.1	12.17	6.61	40.9	2.22	0.	0.
28	21.8	759.1	21.06	11.44	102.7	5.58	0.	0.
29	22.4	774.3	19.92	10.82	71.1	3.86	0.	0.
30	22.3	766.8	25.83	14.03	118.7	6.44	0.	0.

Table 2. Experimental and Predicted Rates of Reaction of Nitrogen Dioxide

Test	Temp.	Press.	Nitrogen Dioxide Concentration	Acetaldehyde Concentration	Rate of Reaction of Nitrogen Dioxide 10^{-11} mol/l.sec	
	^{o}C	mm Hg	10^{-7} mol/l	10^{-3} mol/l	Exper.	Predict
1	22.1	754.7	8.49	4.04	2.895	2.948
2	22.0	757.2	8.21	2.65	1.919	1.870
3	22.3	768.4	12.47	6.88	7.198	7.375
4	21.9	760.9	9.78	6.70	5.650	5.633
5	22.4	765.6	10.71	1.93	1.798	1.777
6	22.0	755.5	8.01	7.98	5.451	5.495
7	21.7	775.1	10.08	1.24	1.099	1.074
8	22.0	759.0	6.77	2.80	1.662	1.630
9	22.0	771.8	6.62	7.06	4.010	4.018
10	22.0	752.8	6.98	7.97	4.739	4.782
11	22.0	772.2	8.44	4.19	3.089	3.040
12	21.8	768.1	6.33	4.36	2.439	2.372
13	21.9	753.6	7.51	4.70	3.101	3.034
14	22.0	760.8	9.41	3.09	2.444	2.500
15	22.6	757.8	7.80	5.68	3.862	3.808
16	22.3	762.7	6.91	5.92	3.418	3.516
17	21.9	768.6	12.81	6.56	7.274	7.224
18	22.0	608.7	11.93	3.76	3.852	3.856
19	22.0	516.6	6.50	3.66	2.046	2.045
20	22.3	407.3	11.91	5.01	5.134	5.129

Table 2, continued

Test	Temp.	Press.	Nitrogen Dioxide Concentration	Acetaldehyde Concentration	Rate of Reaction of Nitrogen Dioxide 10^{-11} mol/l.sec	
	^{o}C	mm Hg	10^{-7} mol/l	10^{-3} mol/l	Exper.	Predict
21	22.2	764.2	9.19	5.18	4.068	4.092
22	22.1	773.4	7.82	5.50	3.660	3.697
23	22.0	757.2	9.89	4.76	3.982	4.047
24	22.5	768.7	8.37	6.20	4.479	4.461
25	21.9	758.6	9.71	4.27	3.471	3.564
26	22.0	761.2	7.20	4.64	2.870	2.872
27	22.3	749.1	6.61	2.22	1.265	1.261
28	21.8	759.1	11.44	5.58	5.586	5.487
29	22.4	774.3	10.82	3.86	3.540	3.590
30	22.3	766.8	14.03	6.44	7.771	7.769

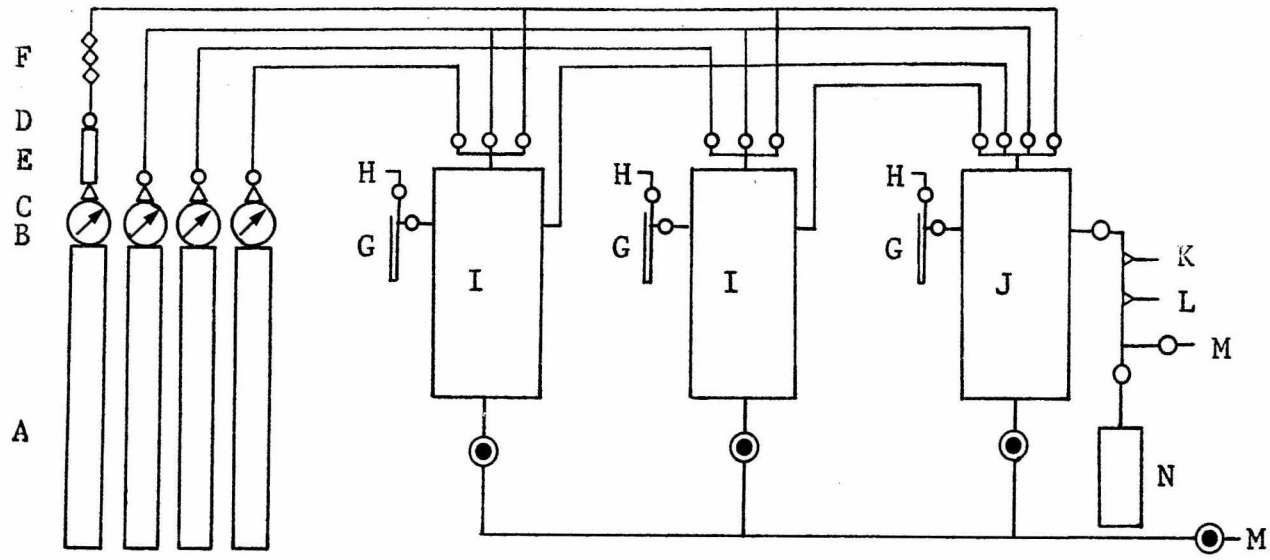
Table 3. The Variation with Temperature of the Initial Second-Order Rate Constant for the Rate of Disappearance of Nitrogen Dioxide

Test	Temp	Press	Nitrogen Dioxide Concentration	Acetaldehyde Concentration	Initial Second-Order Rate Constant
	°C	mm	10^{-7} mol/l	10^{-3} mol/l	liter/mol.sec
101	42.0	763.3	7.31	4.84	3.461×10^{-2}
102	62.4	769.4	7.85	4.36	1.207×10^{-1}
103	86.6	766.1	8.36	3.17	4.419×10^{-1}
104	107.1	766.7	8.28	2.54	1.166
105	122.3	764.4	8.58	1.98	2.244

LIST OF FIGURES

LIST OF FIGURES, continued

LIST OF FIGURES, continued



A Gas Cylinders
B Pressure Regulators
C Check Valves
D Needle Valves
E Molecular Sieve Trap
F Dry Ice-Acetone Trap
G Mercury Manometer
H McLeod Gauge
I Mix Tank

J Reactor
K Sample Loop to Chromatograph
L Sample Loop to Chromatograph
M To Vacuum Pump
N Standard Tank
o 1/8-inch valve
O 1/4-inch valve
◉ 3/4-inch valve

Figure 1. Flow diagram for the experimental equipment.

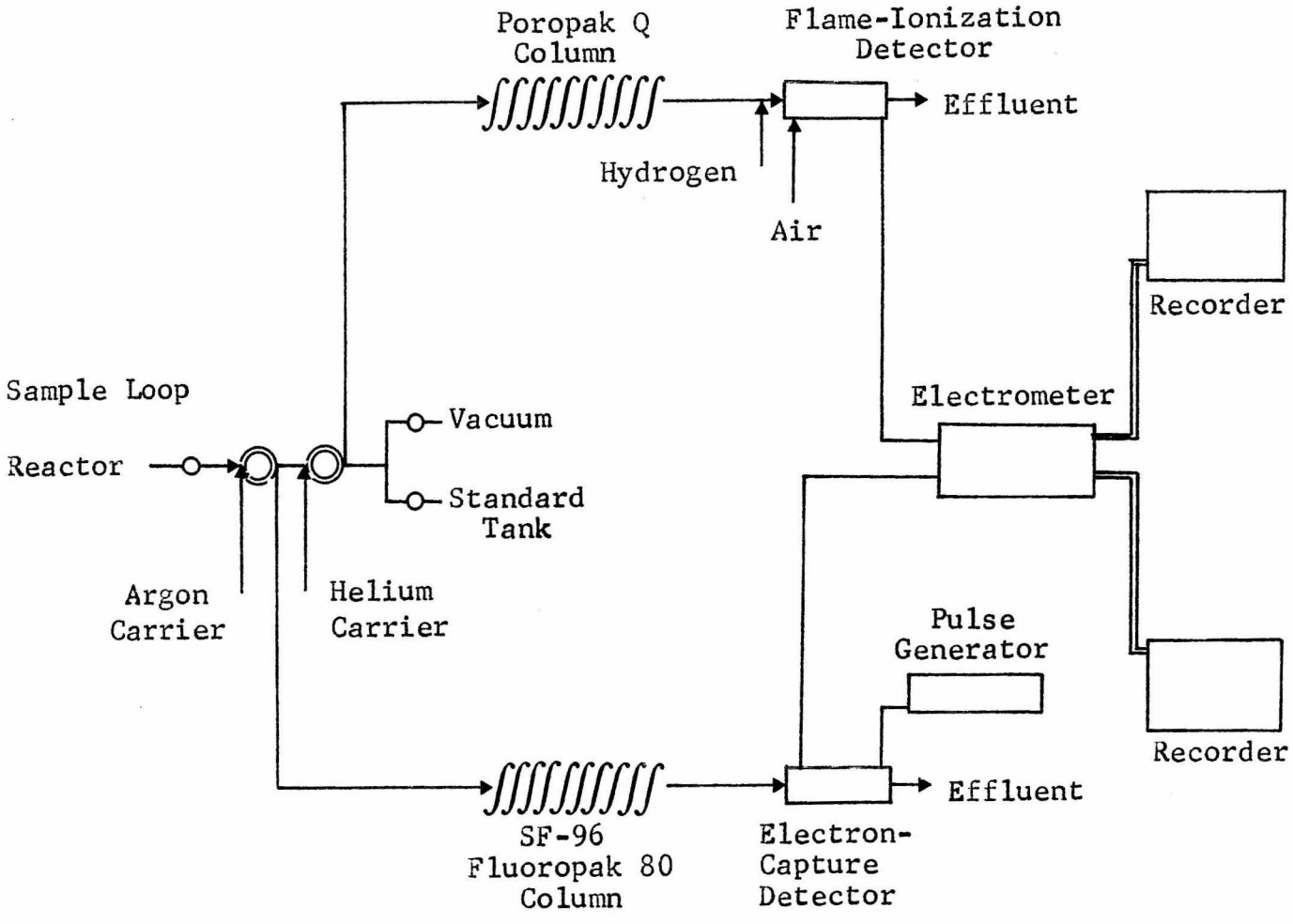


Figure 2. Schematic diagram of the gas chromatograph.

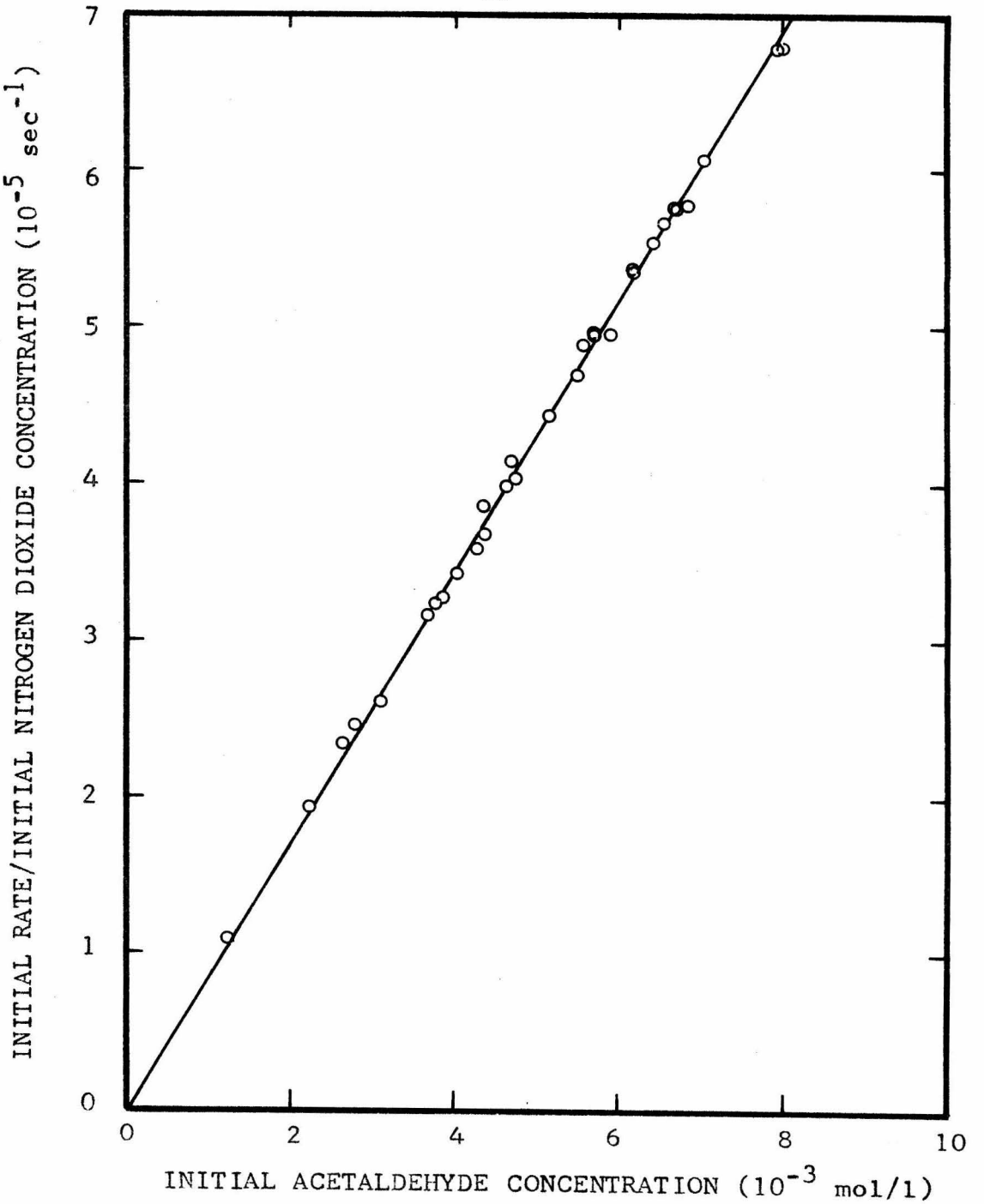


Figure 3. The first order dependence of acetaldehyde in the acetazldehyde-nitrogen dioxide reaction.

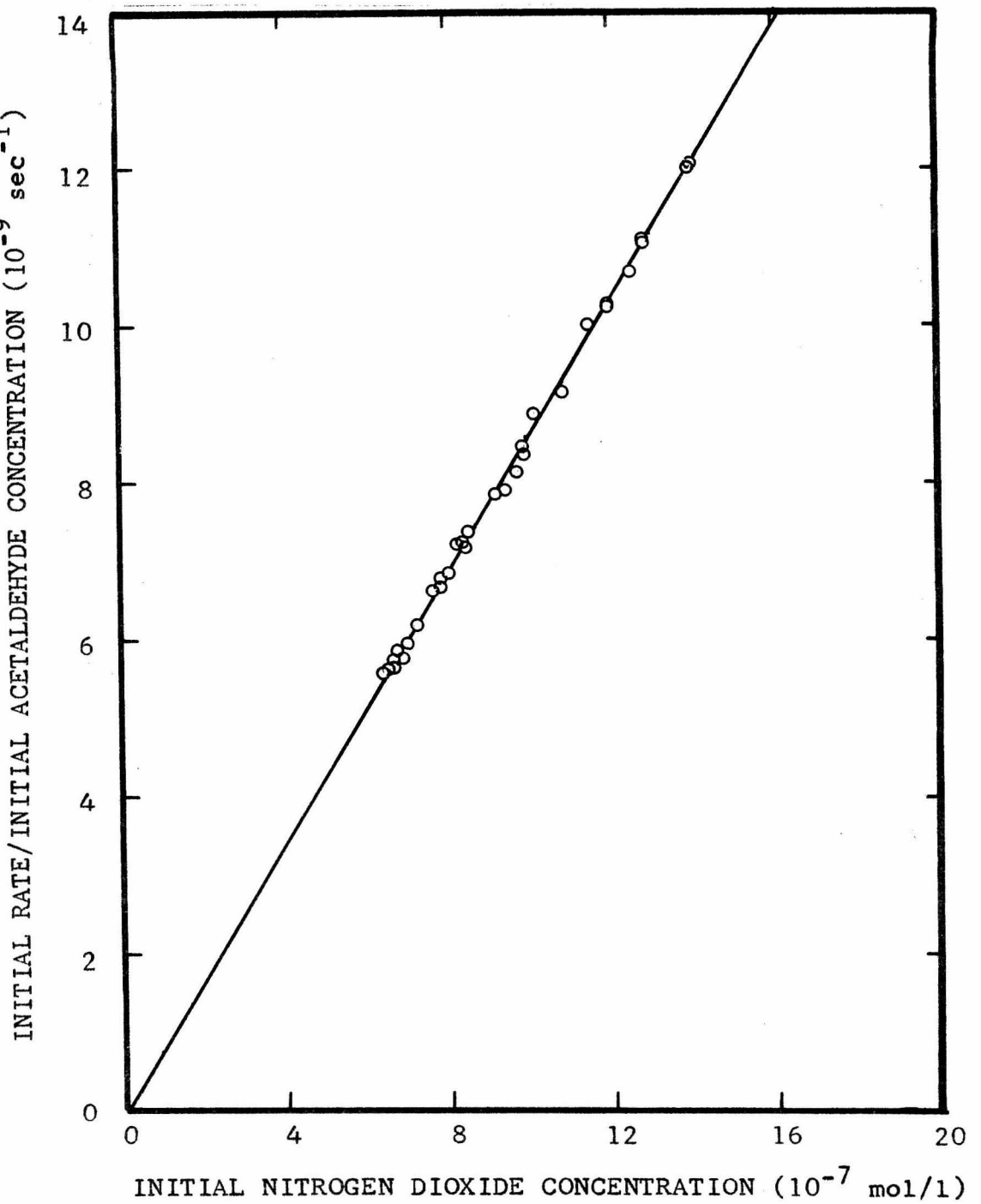


Figure 4. The first-order dependence of nitrogen dioxide in the reaction between acetaldehyde and nitrogen dioxide.

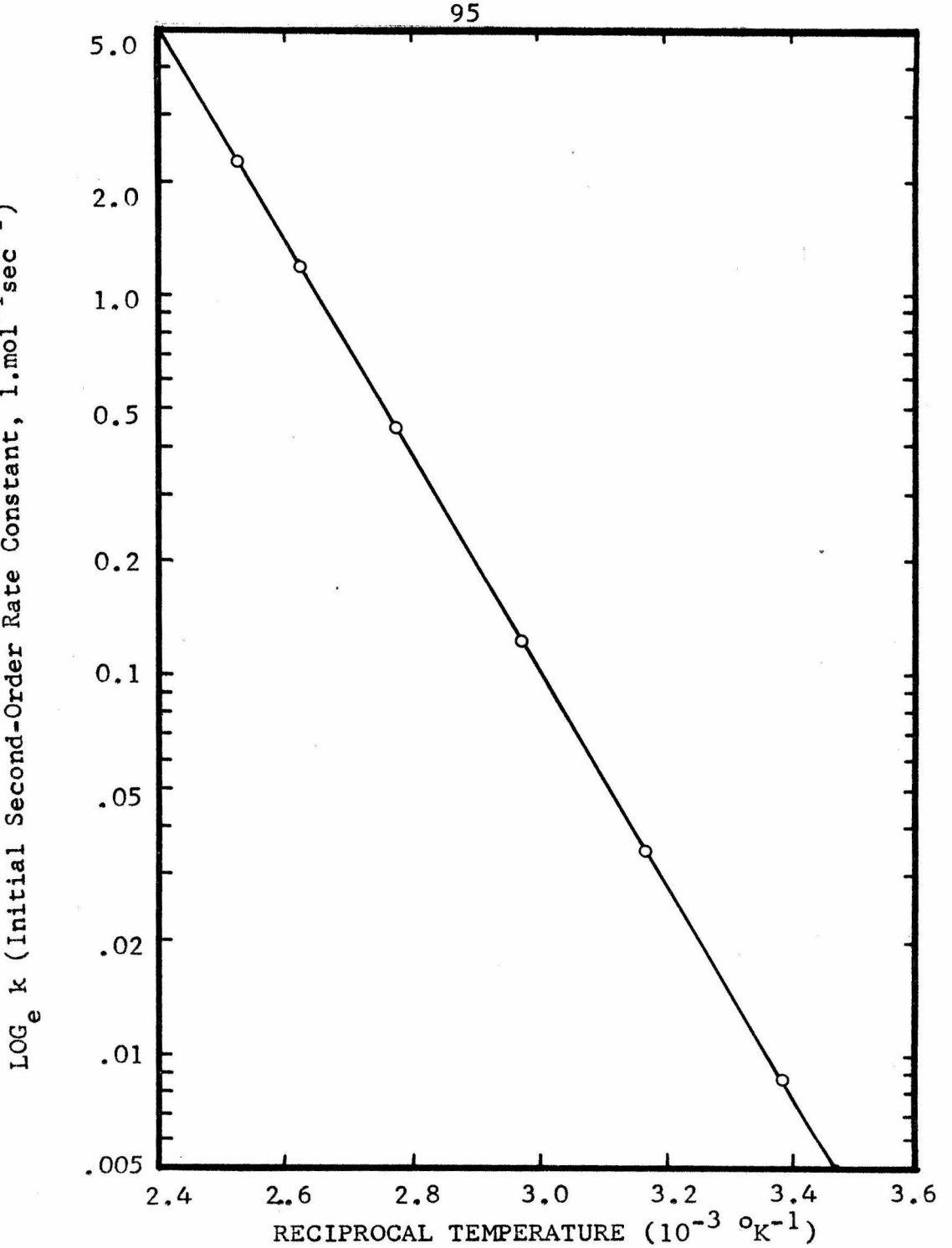


Figure 5. Arrhenius plot for the reaction between acetaldehyde and nitrogen dioxide.

Test 4
Initial Conditions
Reactor Temperature: 21.9°C
Reactor Pressure: 760.9 mm
Acetaldehyde Pressure: 123.3 mm
Nitrogen Dioxide Pressure: 0.01800 mm

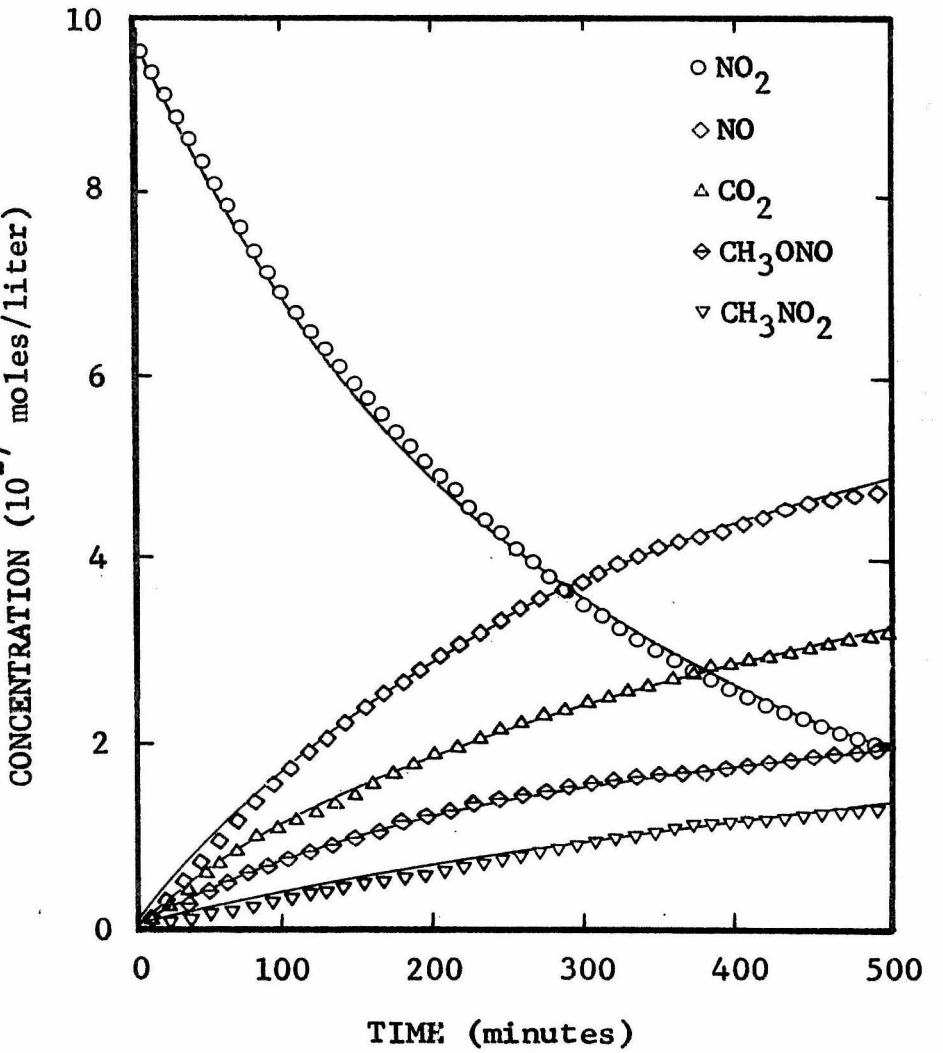


Figure 6. Predicted and experimental concentrations of reactants and products as functions of time for Test 4.

Test 6
Initial Conditions
Reactor Temperature: 22.0°C
Reactor Pressure: 755.5 mm
Acetaldehyde Pressure: 146.9 mm
Nitrogen Dioxide Pressure: 0.01474 mm

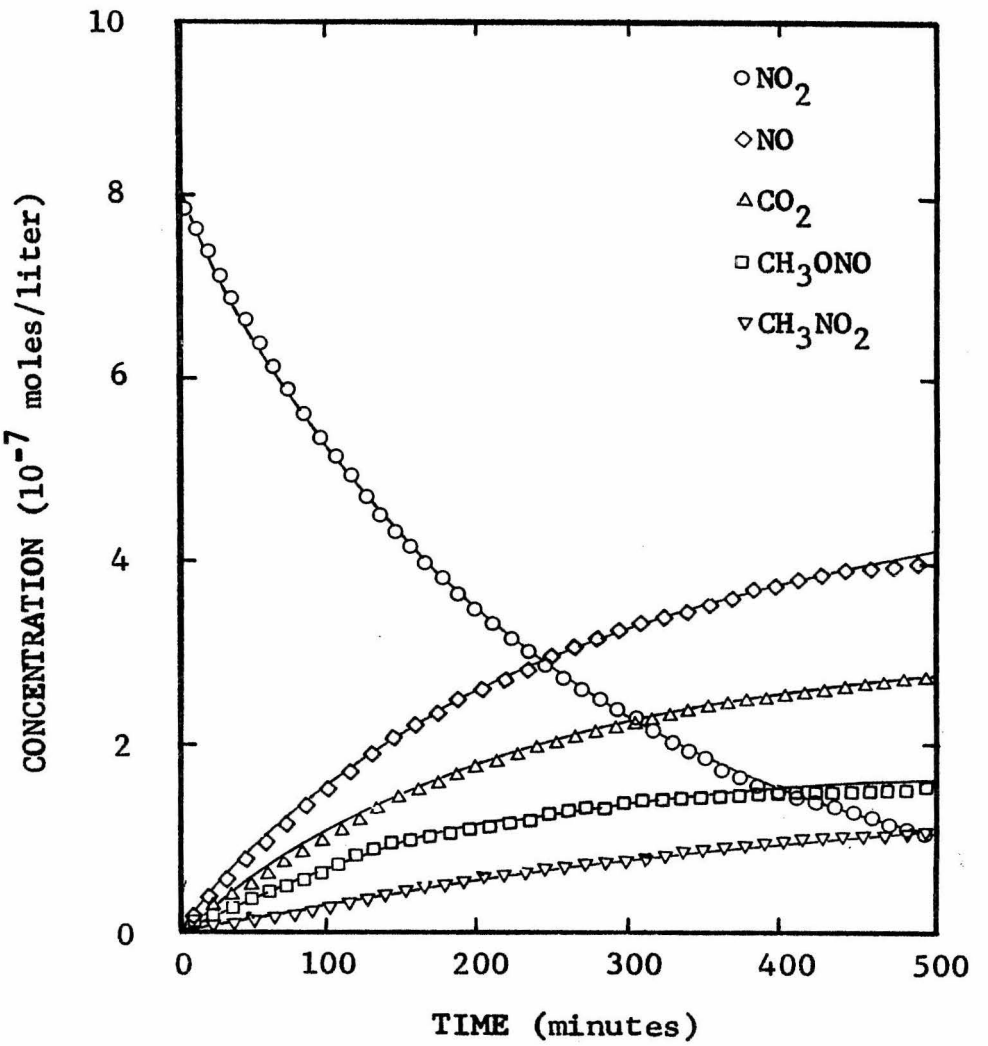


Figure 7. Predicted and experimental concentrations of reactants and products as functions of time for Test 6.

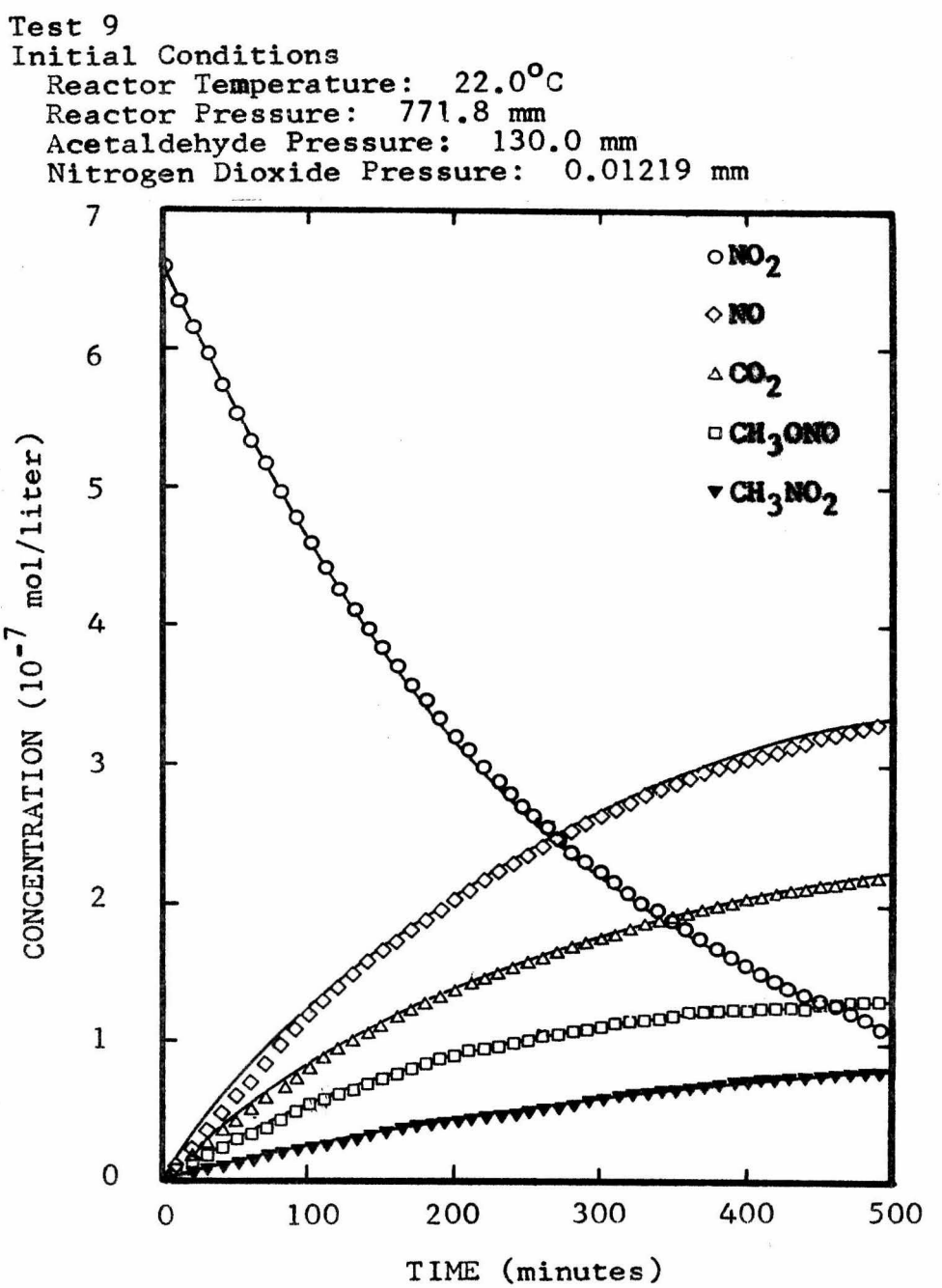


Figure 8. Predicted and experimental concentrations of reactants and products as functions of time for Test 9.

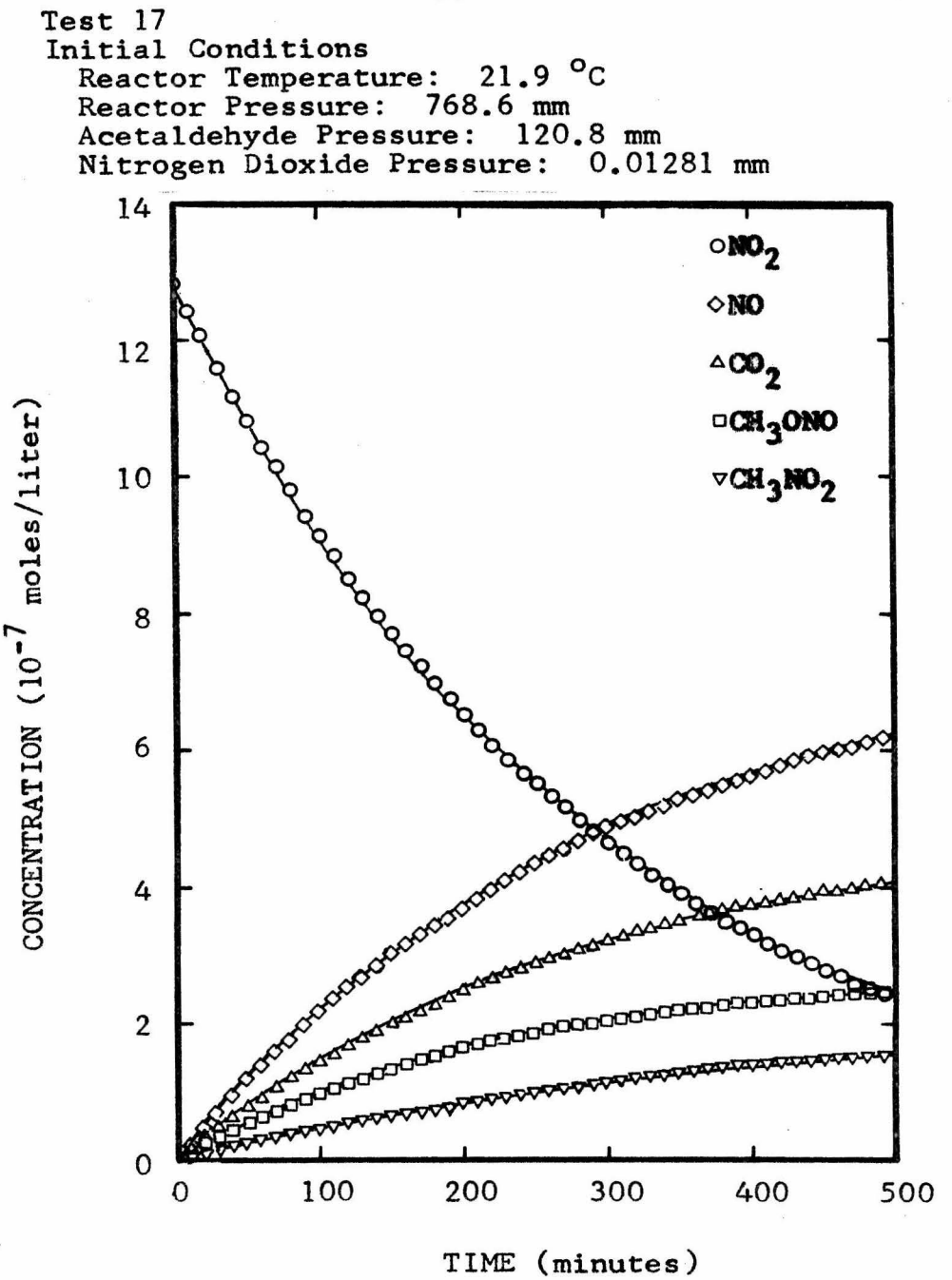


Figure 9. Predicted and experimental concentrations of reactants and products as functions of time for Test 17.

Test 18
Initial Conditions
Reactor Temperature: 22.0°C
Reactor Pressure: 608.7 mm
Acetaldehyde Pressure: 69.2 mm
Nitrogen Dioxide Pressure: 0.02196 mm

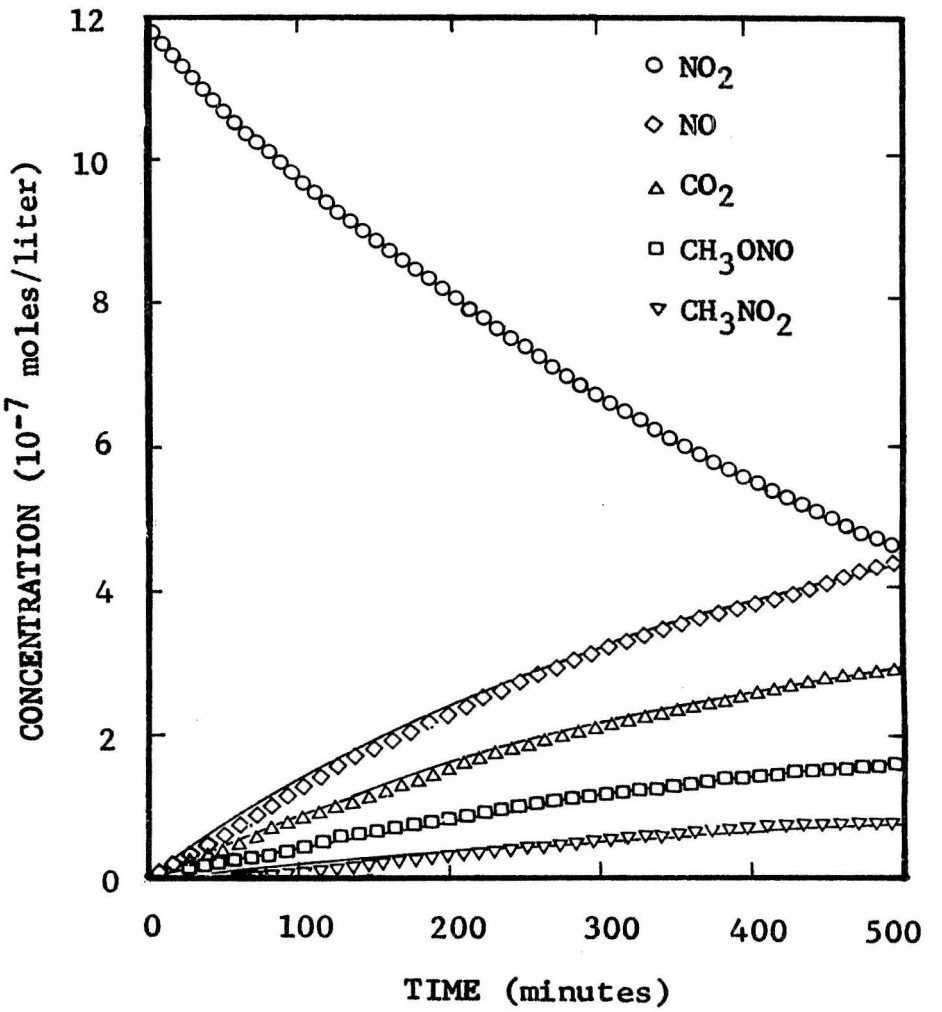


Figure 10. Predicted and experimental concentrations of reactants and products as functions of time for Test 18.

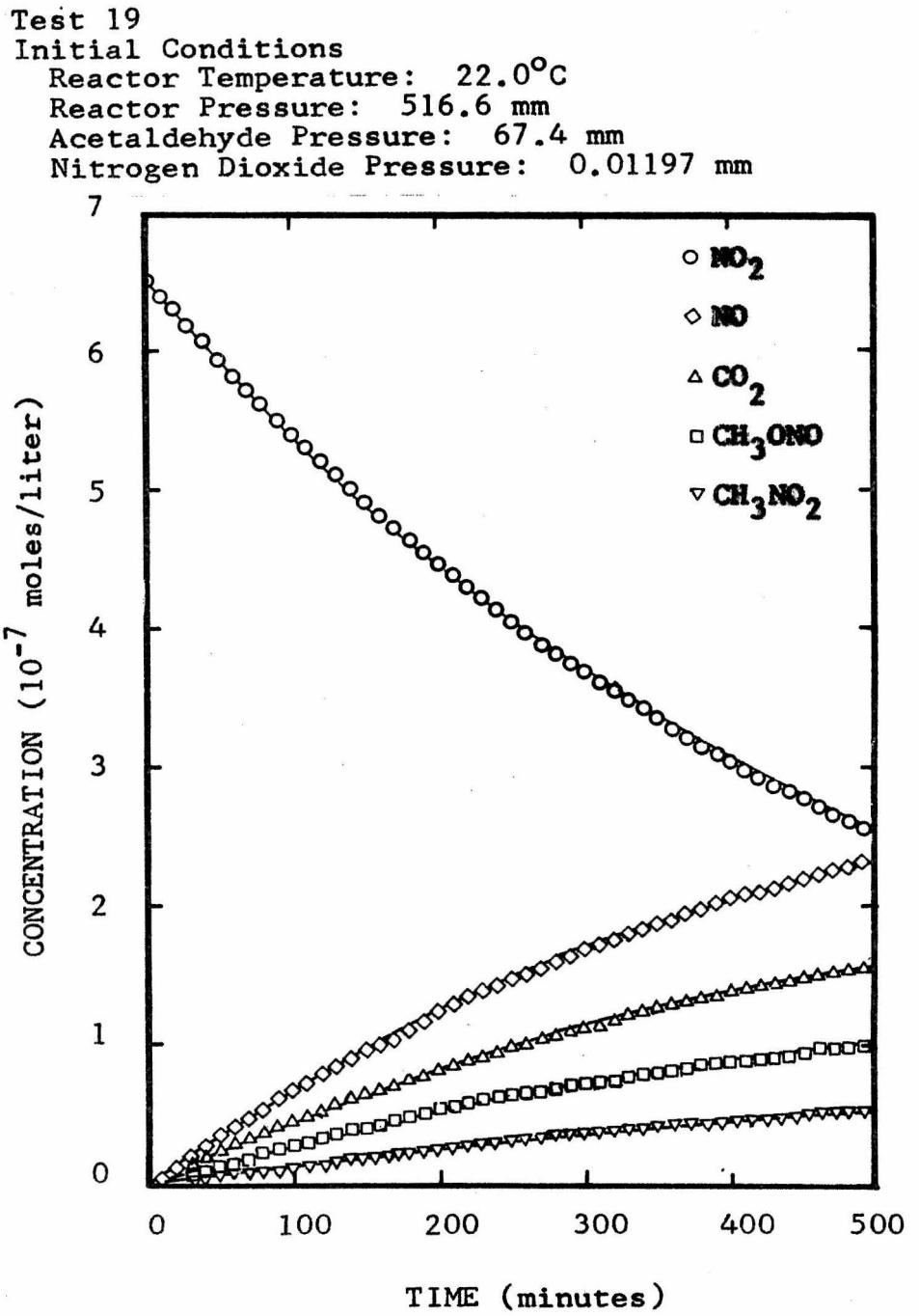


Figure 11. Predicted and experimental concentrations of reactants and products as functions of time for Test 19.

Test 21
Initial conditions
Reactor Temperature: 22.2°C
Reactor Pressure: 773.4 mm
Acetaldehyde Pressure: 95.3 mm
Nitrogen Dioxide Pressure: 0.01692 mm
Nitric Oxide Pressure: 0.000697 mm

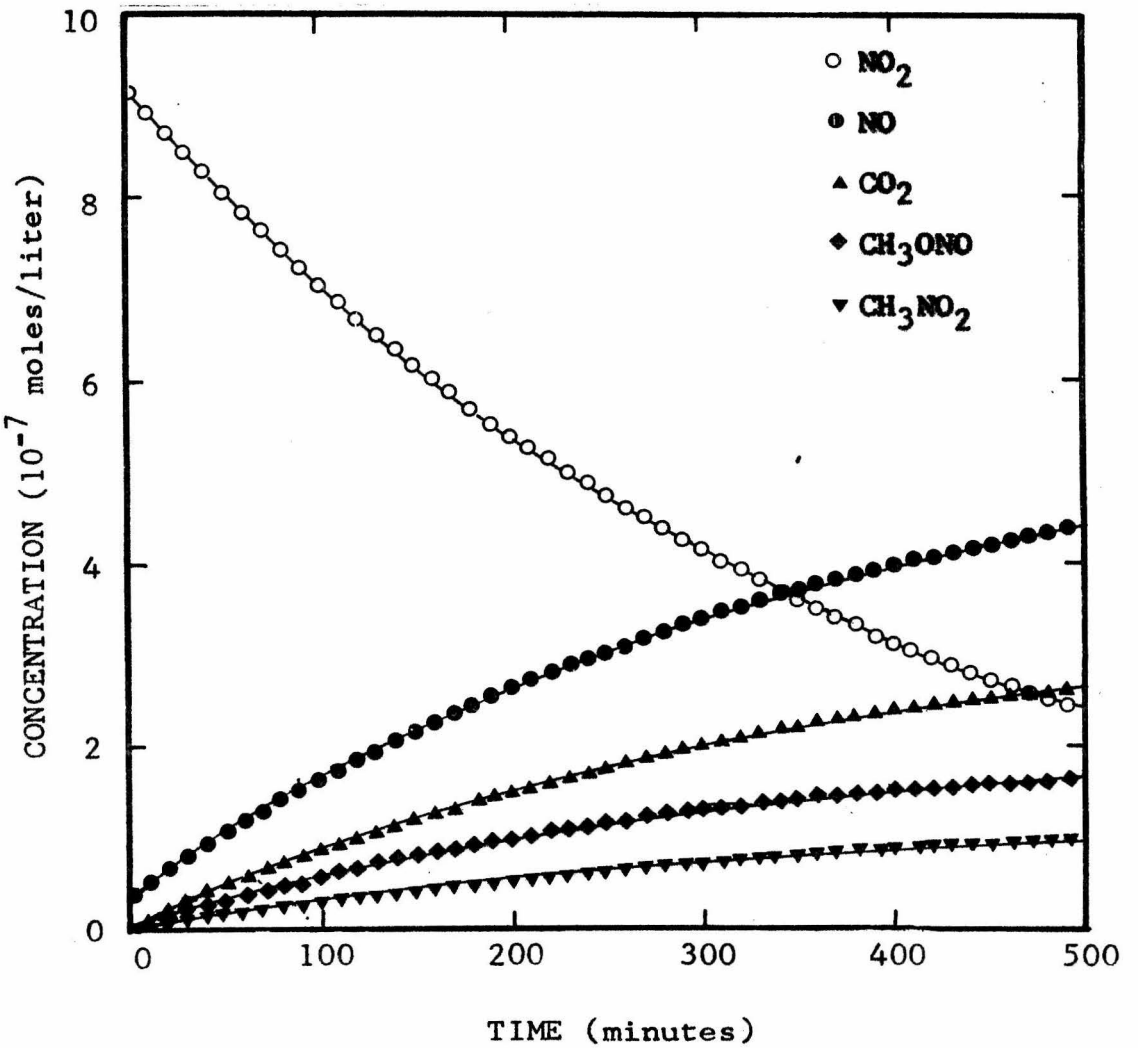


Figure 12. Predicted and experimental concentrations of reactants and products as functions of time for Test 21.

Test 24
Initial Conditions
Reactor Temperature: 22.5°C
Reactor Pressure: 768.7 mm
Acetaldehyde Pressure: 114.2 mm
Nitrogen Dioxide Pressure: 0.01540 mm
Nitric Oxide Pressure: 0.002490

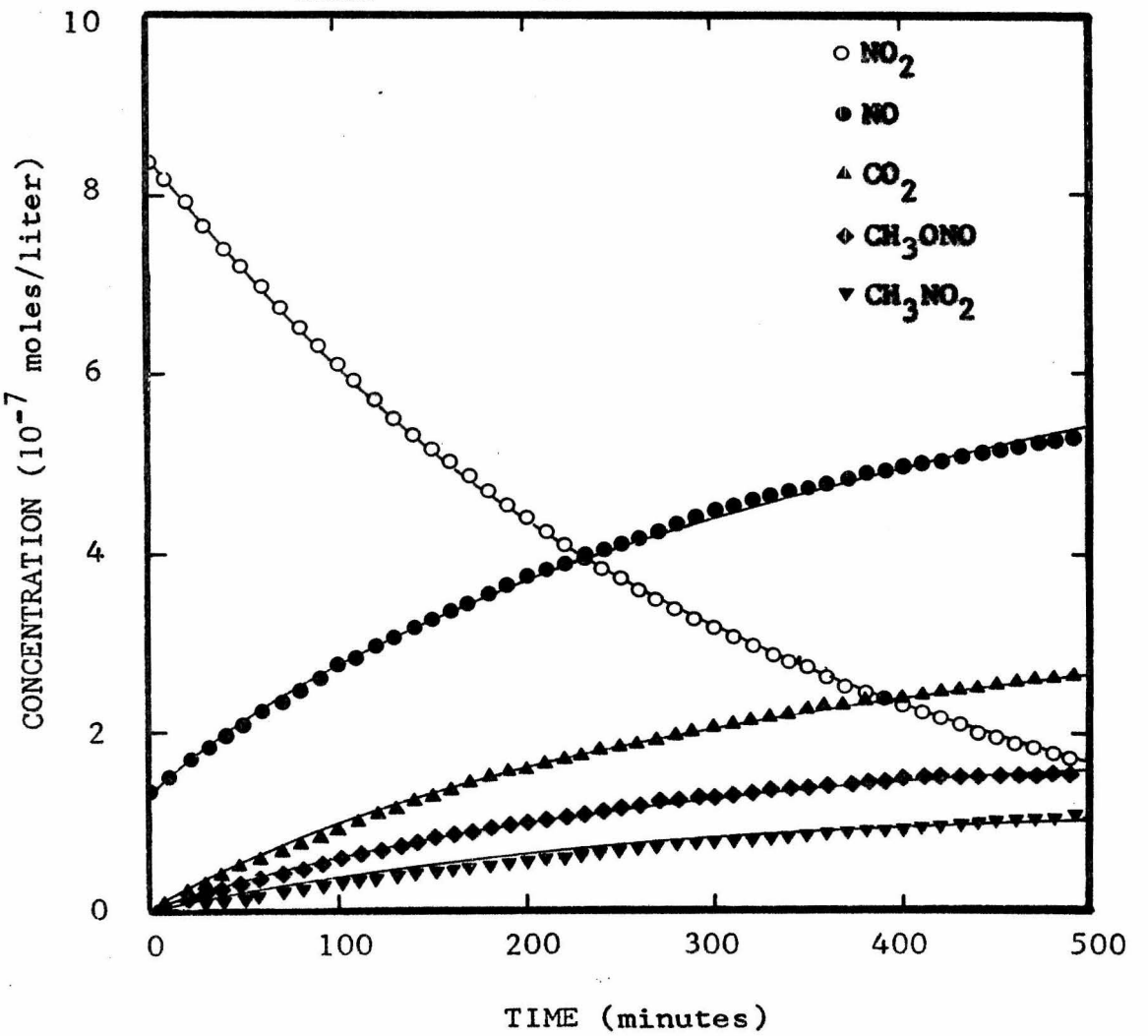


Figure 13. Predicted and Experimental concentration of reactants and products as functions of time for Test 24.

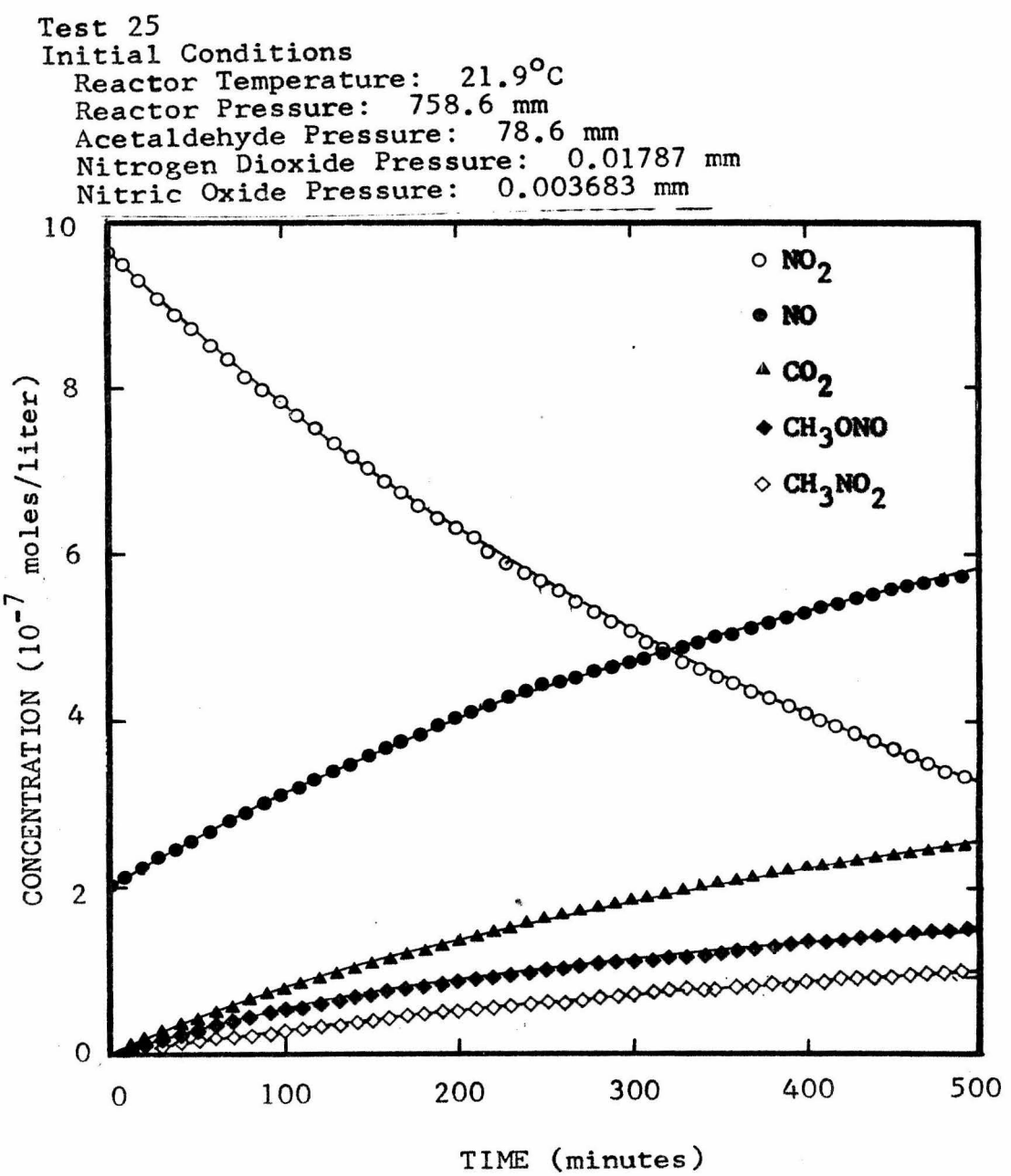


Figure 14. Predicted and experimental concentrations of reactants and products as functions of time for Test 25.

Test 27
Initial Conditions
Reactor Temperature: 22.3°C
Reactor Pressure: 749.1 mm
Acetaldehyde Pressure: 40.9 mm
Nitrogen Dioxide Pressure: 0.01217 mm
Glass Beads in the Reactor

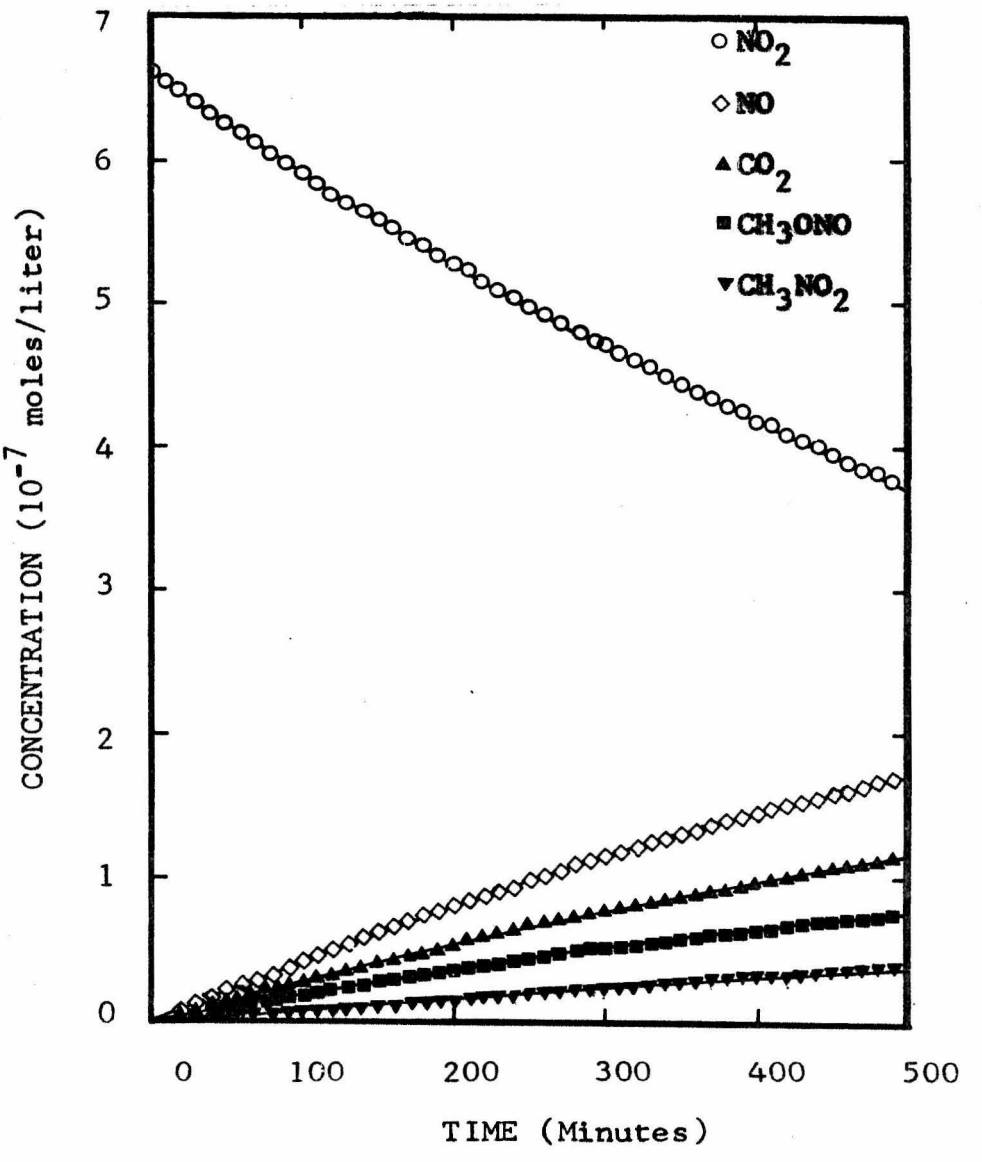


Figure 15. Predicted and experimental concentrations of reactants and products as functions of time for Test 27.

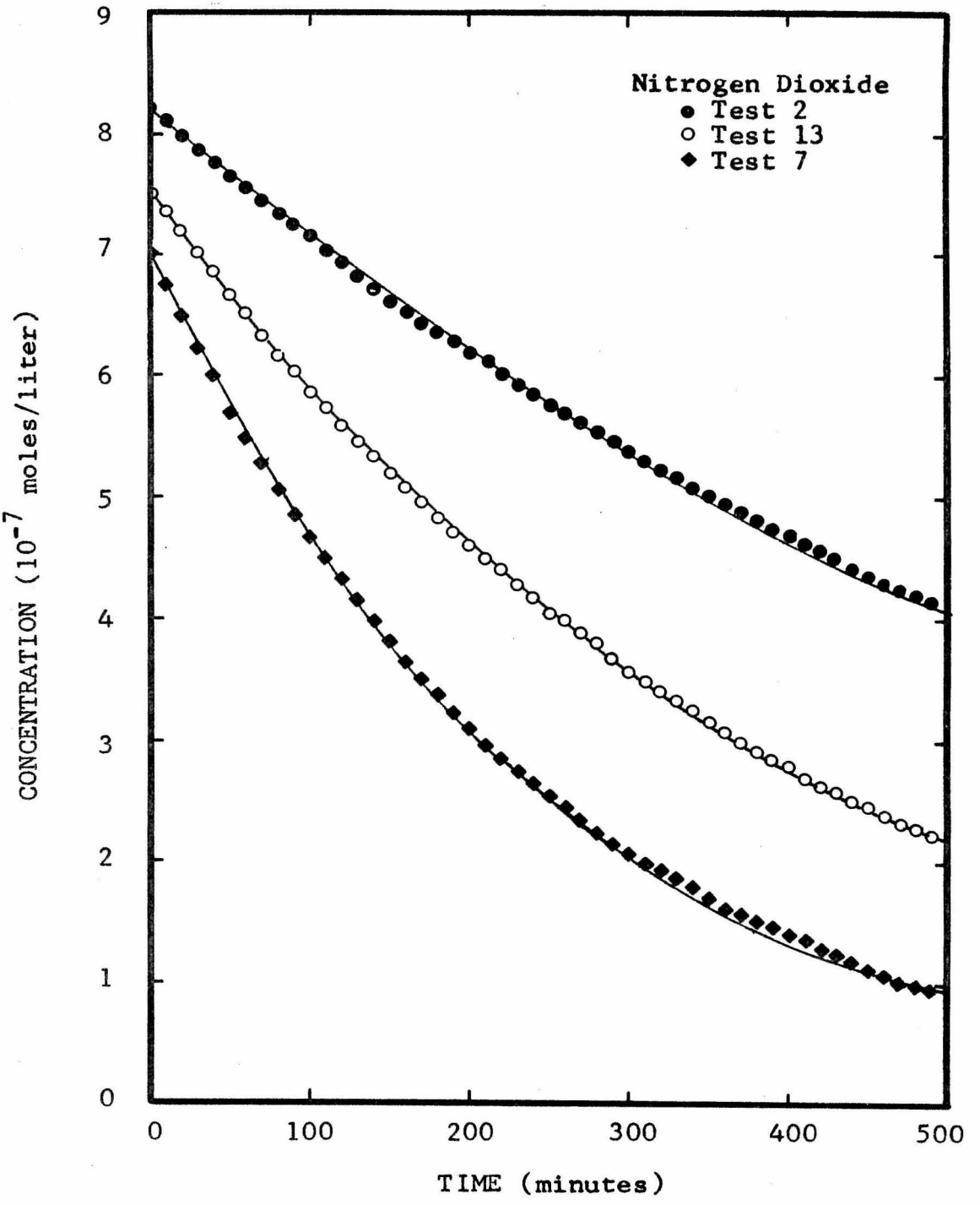


Figure 16. Predicted and experimental concentrations of nitrogen dioxide as functions of time for Tests 2, 7 and 13.

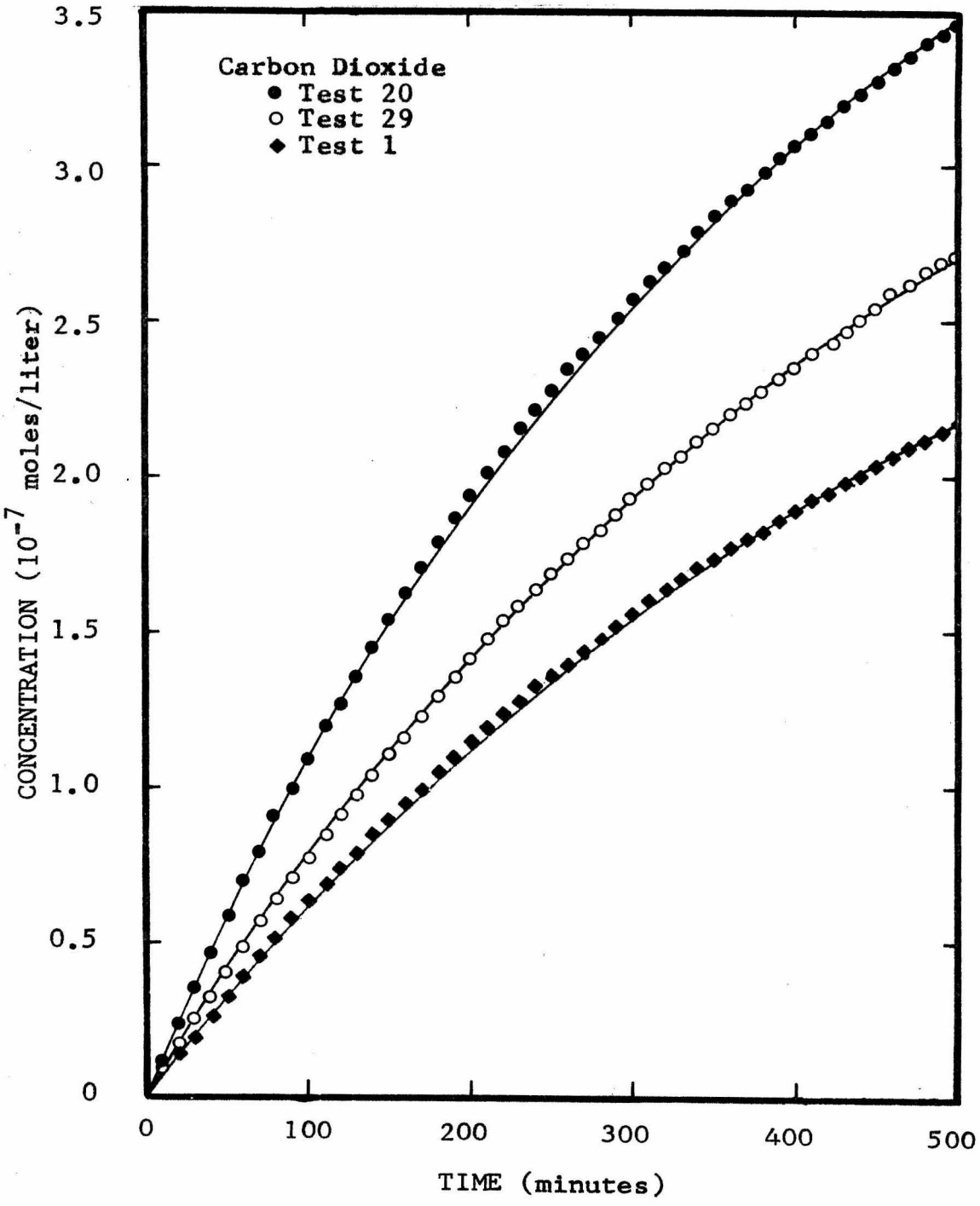


Figure 17. Predicted and experimental concentrations of carbon dioxide as functions of time for Tests 1, 20 and 29.

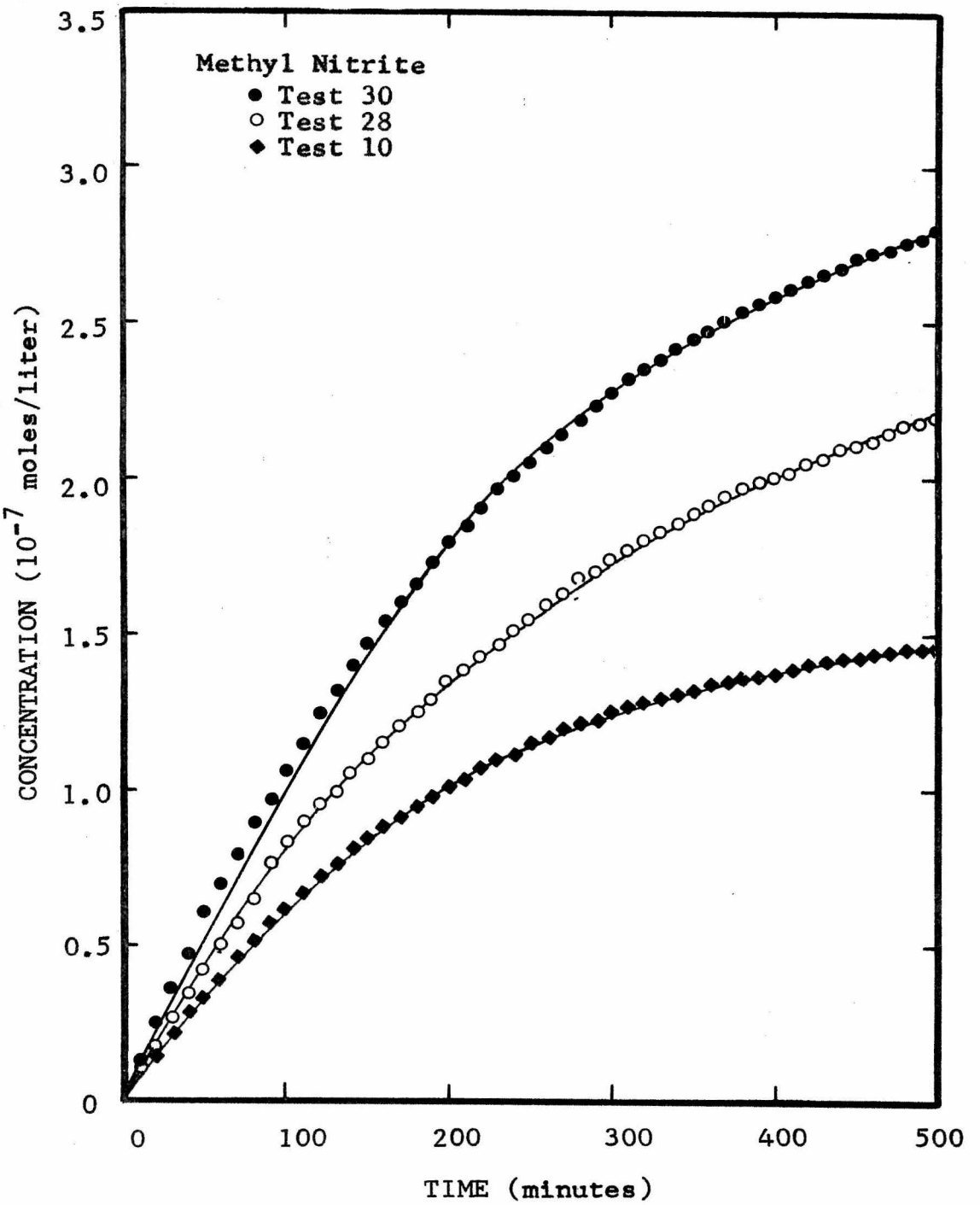


Figure 18. Predicted and experimental concentrations of methyl nitrite as functions of time for Tests 10, 28 and 30.

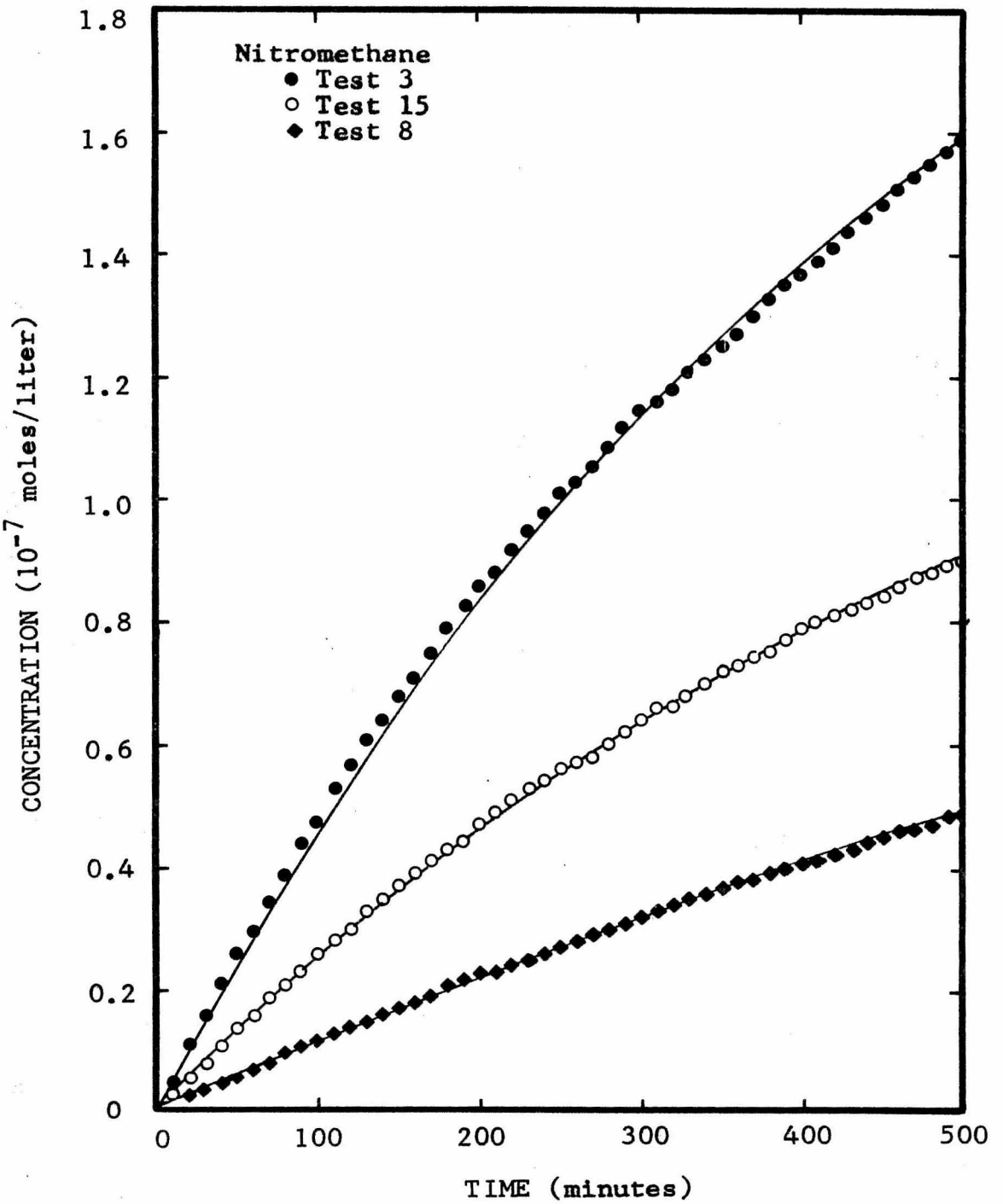


Figure 19. Predicted and experimental concentrations of nitromethane as functions of time for Tests 3, 8 and 15.

Test 25
Initial Conditions
Reactor Temperature: 21.9°C
Reactor Pressure: 758.6 mm
Acetaldehyde Pressure: 78.6 mm
Nitrogen Dioxide Pressure: 0.01787 mm
Nitric Oxide Pressure: 0.003683 mm

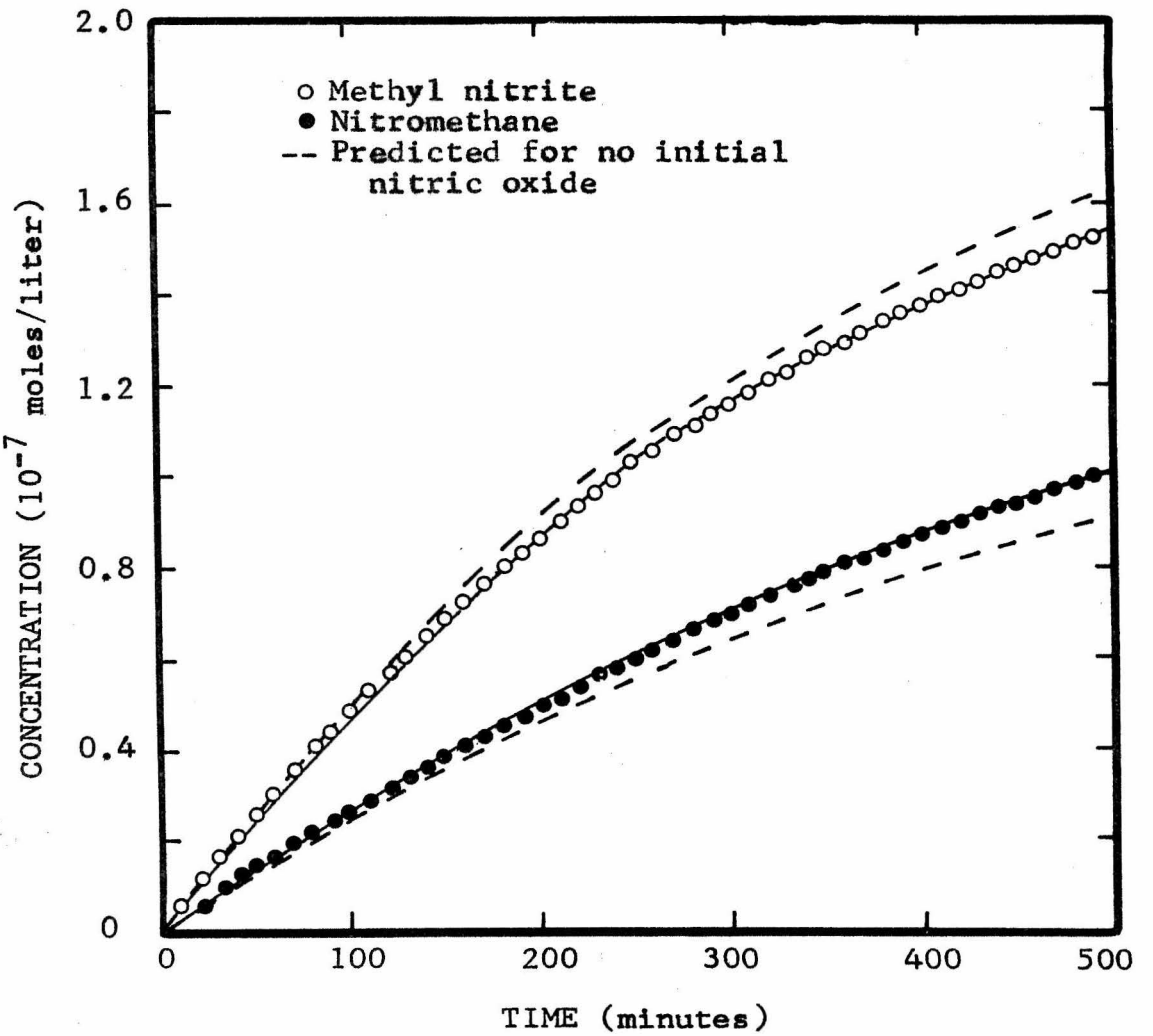


Figure 20. Concentrations of methyl nitrite and nitromethane as functions of time for Test 25; experimental, predicted, and predicted for no initial nitric oxide.

Test 23
Initial Conditions
Reactor Temperature: 22.0°C
Reactor Pressure: 757.2 mm
Acetaldehyde Presssure: 87.7 mm
Nitrogen Dioxide Pressure: 0.01821 mm
Nitric Oxide Pressure: 0.002238 mm

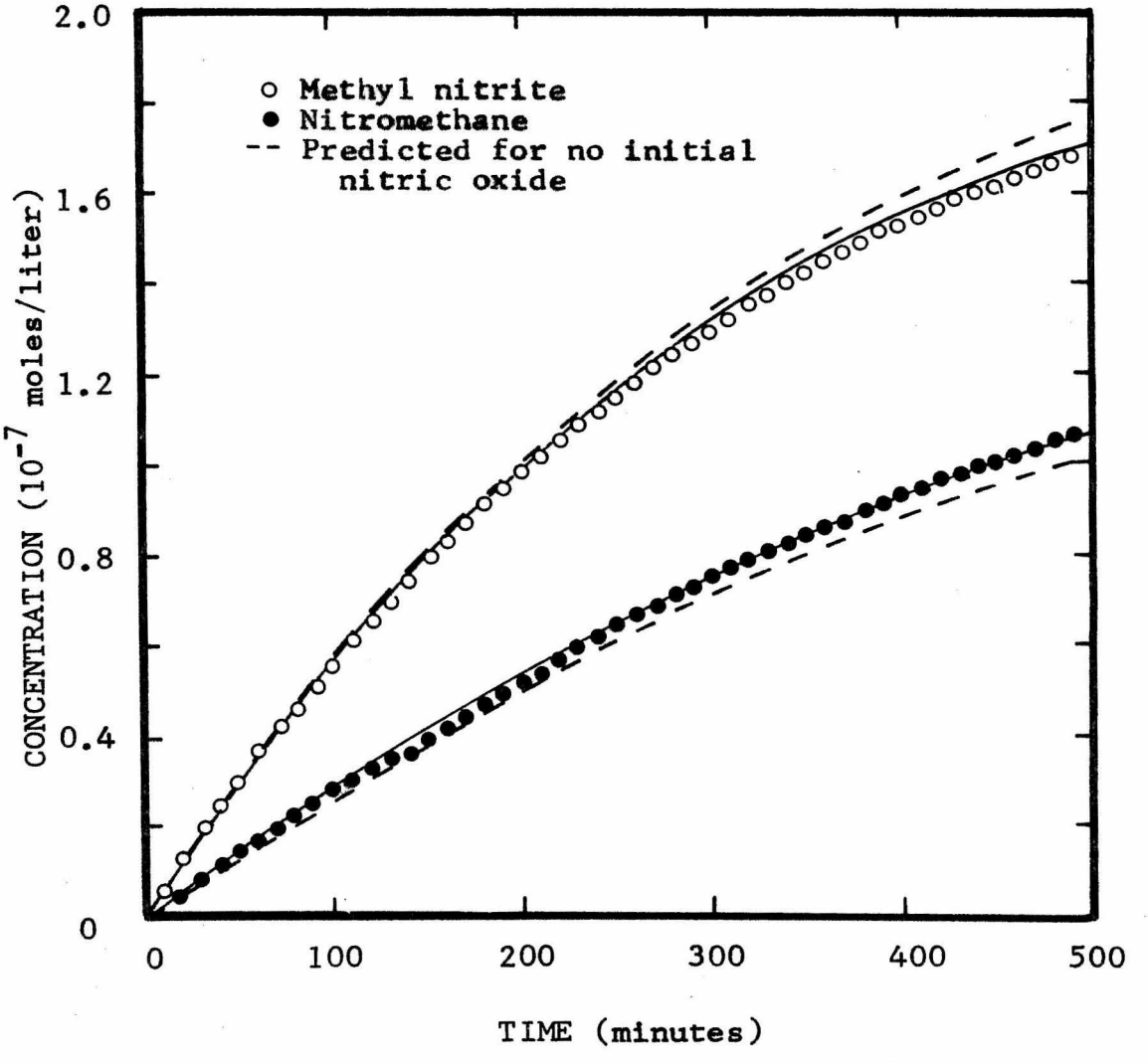


Figure 21. Concentrations of methyl nitrite and nitromethane as functions of time for Test 23; experimental, predicted, and predicted for no initial nitric oxide.

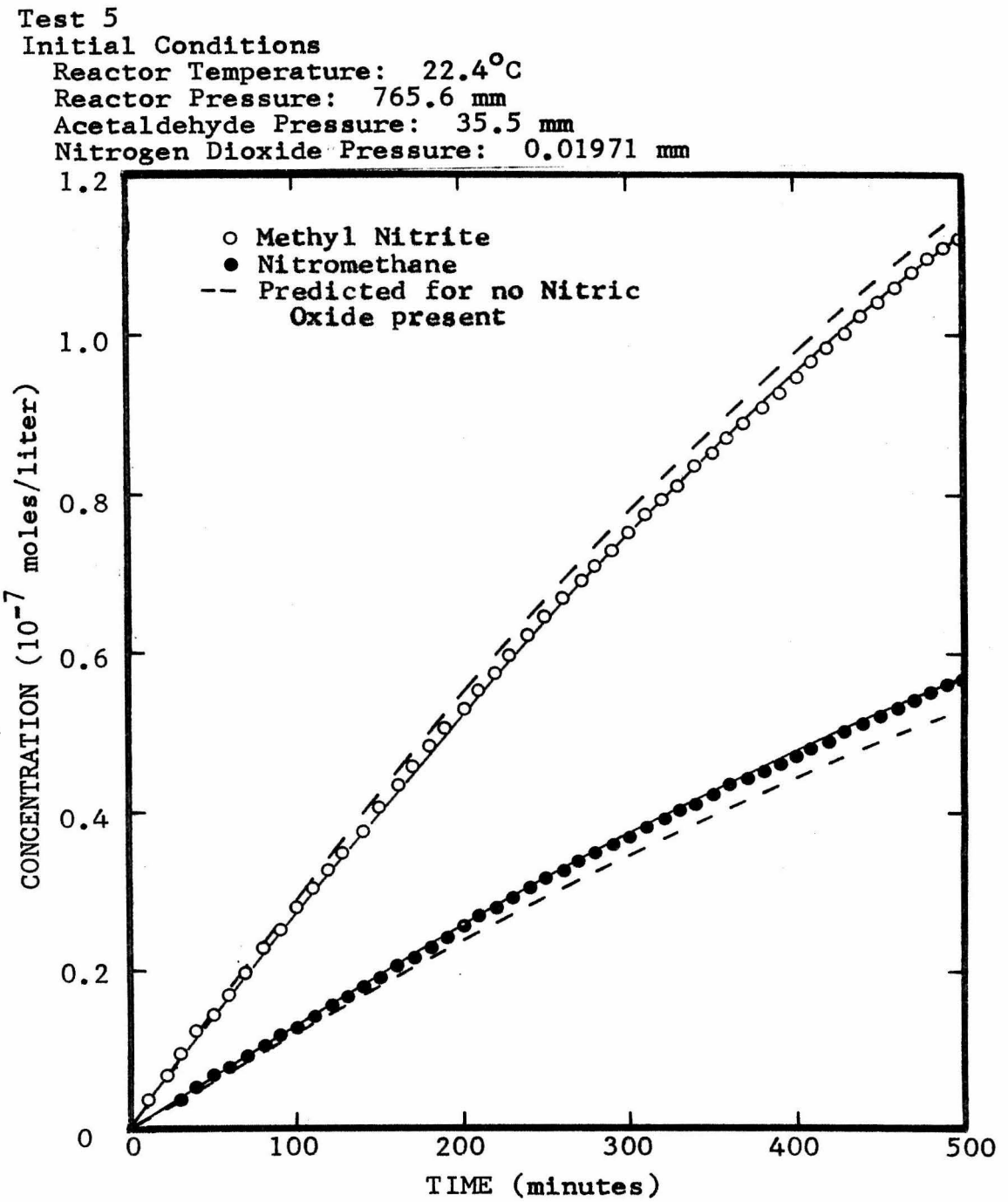


Figure 22. Concentrations of methyl nitrite and nitromethane as functions of time for Test 5; experimental, predicted, and predicted for no nitric oxide.

Test 14
Initial Conditions
Reactor Temperature: 22.0°C
Reactor Pressure: 760.8 mm
Acetaldehyde Pressure: 56.9 mm
Nitrogen Dioxide Pressure: 0.01732 mm

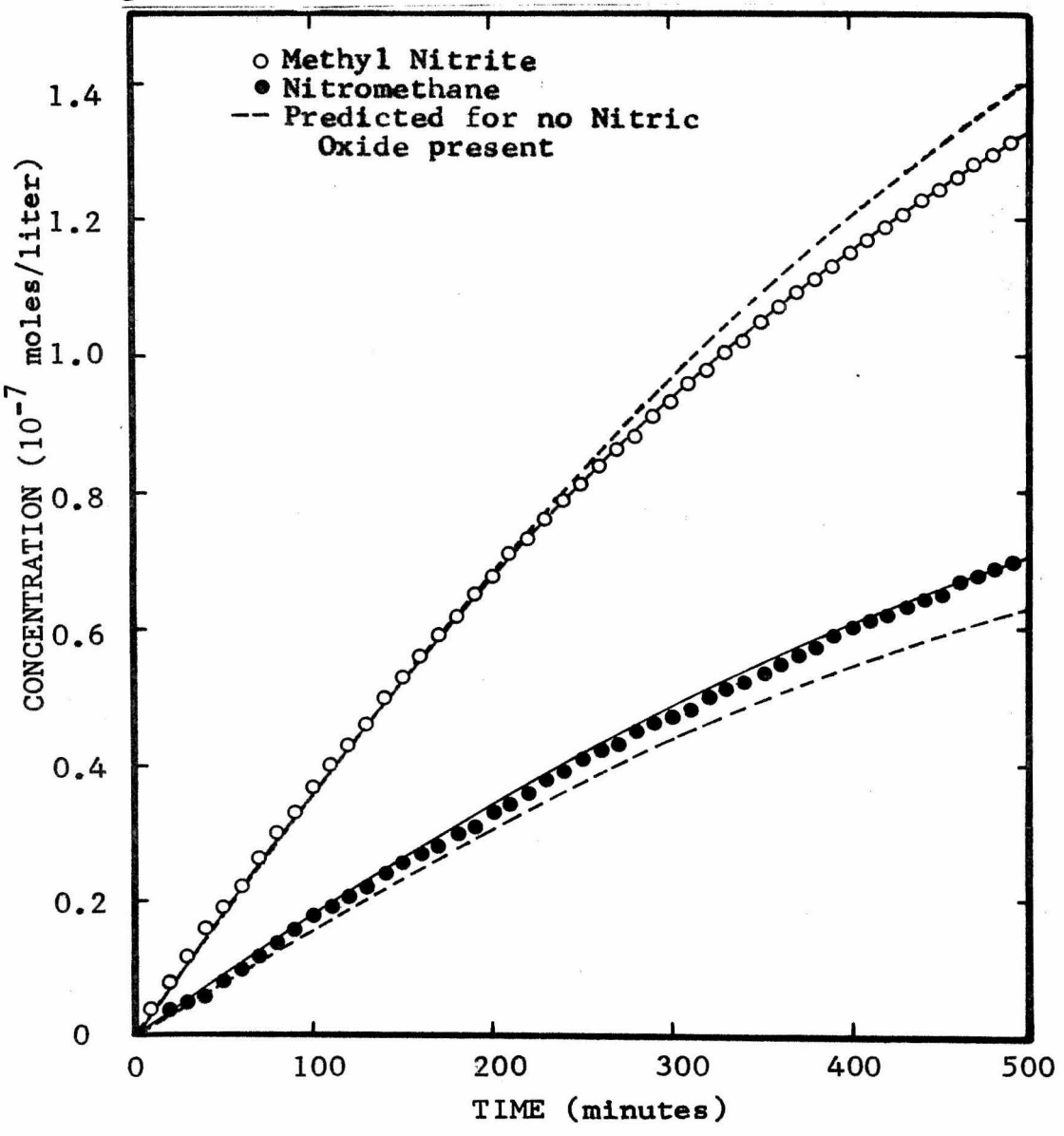


Figure 23. Concentrations of methyl nitrite and nitromethane as functions of time for Test 14; experimental, predicted, and predicted for no nitric oxide.

Test 22
Initial Conditions
Acetaldehyde Pressure: 101.3 mm
Nitrogen Dioxide Pressure: 0.01439 mm
Nitric Oxide Pressure: 0.001196 mm

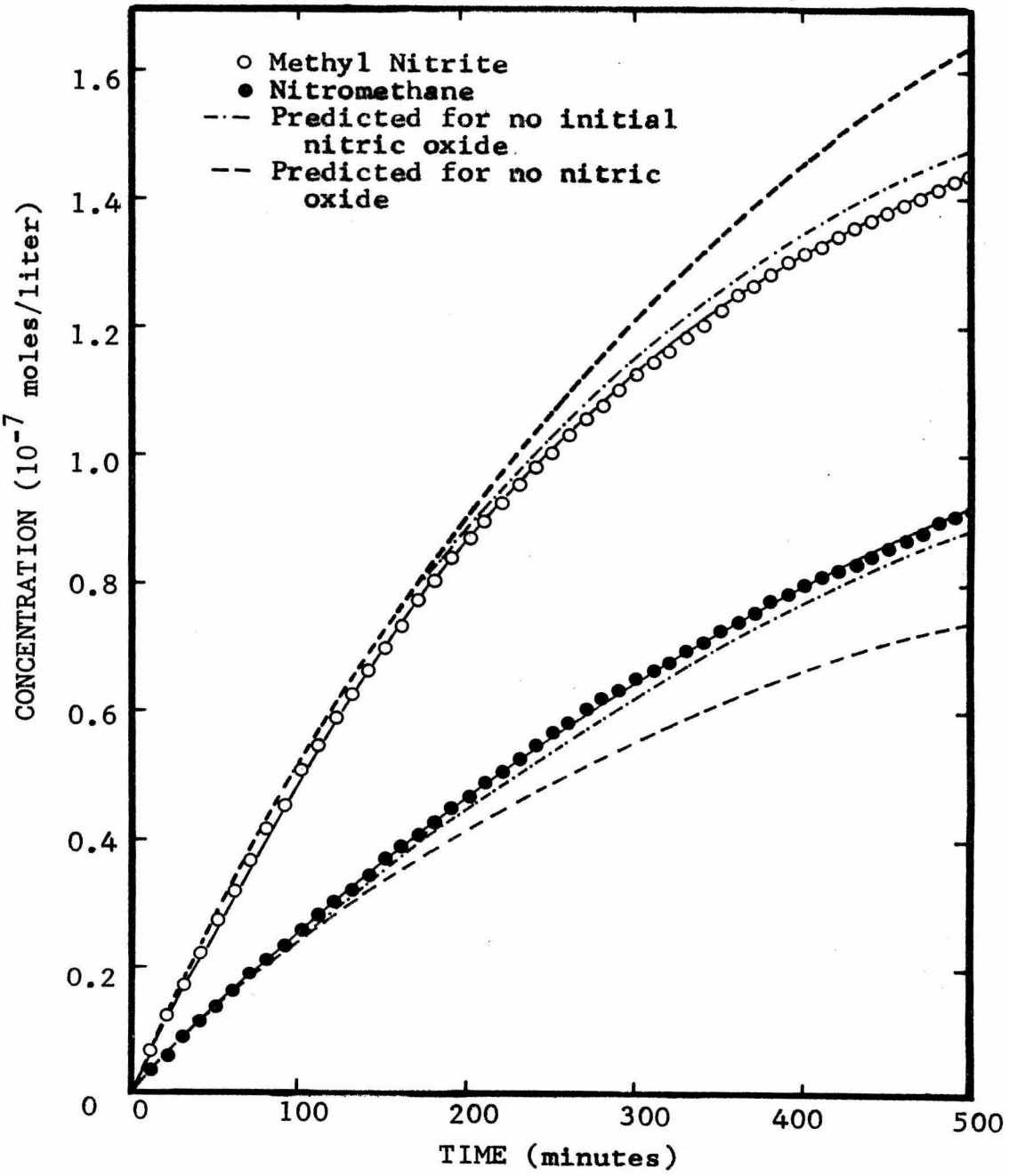


Figure 24. Concentrations of methyl nitrite and nitromethane as functions of time for Test 22; experimental, predicted, predicted for no initial nitric oxide, and predicted for no nitric oxide.

APPENDIX A

The concentration-time data for nitrogen dioxide, nitric oxide, carbon dioxide, methyl nitrite and nitromethane are presented for Tests 1 through 30.

All concentrations are given at a temperature of 22.0°C and at the pressure of the reaction.

All pressures are given in millimeters of mercury and at a temperature of 22.0°C.

Test 1
Initial Conditions
Reactor Temperature: 22.1°C
Reactor Pressure: 754.7 mm
Acetaldehyde Pressure: 74.4 mm
Nitrogen Dioxide Pressure: 0.01563 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	8.49	0.	0.	0.	0.
10	8.32	0.10	0.07	0.05	0.02
20	8.15	0.20	0.14	0.09	0.04
30	7.98	0.30	0.20	0.14	0.06
40	7.82	0.39	0.26	0.18	0.09
50	7.66	0.50	0.30	0.22	0.11
60	7.52	0.59	0.39	0.27	0.13
70	7.36	0.68	0.45	0.31	0.15
80	7.22	0.77	0.51	0.35	0.17
90	7.05	0.86	0.57	0.39	0.18
100	6.93	0.94	0.63	0.42	0.20
110	6.79	1.03	0.68	0.46	0.22
120	6.63	1.11	0.74	0.50	0.24
130	6.51	1.20	0.79	0.53	0.26
140	6.38	1.27	0.85	0.57	0.28
150	6.25	1.37	0.90	0.60	0.29
160	6.13	1.42	0.95	0.64	0.31
170	6.00	1.50	1.00	0.67	0.33
180	5.87	1.58	1.05	0.70	0.35
190	5.76	1.63	1.09	0.73	0.36
200	5.65	1.70	1.13	0.76	0.38
210	5.52	1.79	1.19	0.79	0.40
220	5.41	1.85	1.22	0.82	0.41
230	5.30	1.91	1.27	0.85	0.43
240	5.20	1.98	1.32	0.88	0.44
250	5.08	2.05	1.37	0.90	0.46
260	4.99	2.09	1.39	0.93	0.47
270	4.89	2.16	1.43	0.95	0.49
280	4.79	2.21	1.47	0.98	0.50
290	4.68	2.26	1.53	1.00	0.52
300	4.60	2.37	1.56	1.03	0.53

Test 1, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	4.50	2.39	1.60	1.05	0.55
320	4.40	2.45	1.62	1.07	0.56
330	4.31	2.39	1.67	1.09	0.57
340	4.23	2.55	1.70	1.12	0.59
350	4.16	2.60	1.74	1.14	0.60
360	4.06	2.66	1.77	1.16	0.61
370	3.98	2.70	1.80	1.18	0.63
380	3.89	2.75	1.84	1.20	0.64
390	3.82	2.79	1.87	1.22	0.65
400	3.75	2.85	1.90	1.23	0.66
410	3.68	2.89	1.94	1.25	0.68
420	3.59	2.94	1.97	1.27	0.69
430	3.51	2.97	1.99	1.29	0.70
440	3.44	3.02	2.02	1.30	0.71
450	3.37	3.07	2.04	1.32	0.72
460	3.31	3.11	2.06	1.34	0.74
470	3.25	3.15	2.10	1.35	0.75
480	3.19	3.19	2.12	1.37	0.76
490	3.12	3.22	2.15	1.38	0.77
500	3.04	3.26	2.18	1.40	0.78

Test 2
Initial Conditions
Reactor Temperature: 22.0°C
Reactor Pressure: 757.2 mm
Acetaldehyde Pressure: 48.4 mm
Nitrogen Dioxide Pressure: 0.01511 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	8.21	0.	0.	0.	0.
10	8.10	0.07	0.05	0.03	0.01
20	7.98	0.14	0.09	0.06	0.03
30	7.86	0.20	0.14	0.09	0.04
40	7.76	0.27	0.18	0.12	0.06
50	7.65	0.33	0.22	0.15	0.07
60	7.55	0.40	0.27	0.18	0.08
70	7.44	0.46	0.31	0.21	0.10
80	7.35	0.52	0.36	0.24	0.11
90	7.24	0.58	0.40	0.26	0.12
100	7.16	0.64	0.44	0.29	0.14
110	7.04	0.70	0.47	0.32	0.15
120	6.94	0.76	0.51	0.34	0.16
130	6.83	0.82	0.55	0.37	0.18
140	6.75	0.87	0.58	0.40	0.19
150	6.65	0.93	0.62	0.42	0.20
160	6.55	0.98	0.66	0.45	0.21
170	6.48	1.05	0.70	0.47	0.23
180	6.38	1.10	0.73	0.49	0.24
190	6.30	1.14	0.77	0.52	0.25
200	6.20	1.20	0.80	0.54	0.26
210	6.12	1.27	0.84	0.56	0.27
220	6.02	1.31	0.86	0.59	0.29
230	5.95	1.36	0.91	0.61	0.30
240	5.86	1.41	0.94	0.63	0.31
250	5.78	1.46	0.97	6.51	0.32
260	5.69	1.51	0.99	0.67	0.33
270	5.62	1.55	1.04	0.69	0.34
280	5.54	1.60	1.07	0.71	0.35
290	5.47	1.65	1.10	0.73	0.36
300	5.38	1.68	1.13	0.75	0.38

Test 2, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	5.32	1.74	1.16	0.77	0.39
320	5.23	1.77	1.19	0.79	0.40
330	5.18	1.82	1.22	0.81	0.41
340	5.10	1.87	1.25	0.83	0.42
350	5.03	1.90	1.27	0.85	0.43
360	4.96	1.95	1.29	0.86	0.44
370	4.89	1.99	1.33	0.88	0.45
380	4.82	2.03	1.36	0.90	0.46
390	4.74	2.08	1.38	0.92	0.47
400	4.69	2.11	1.42	0.93	0.48
410	4.61	2.15	1.44	0.95	0.49
420	4.56	2.19	1.46	0.96	0.50
430	4.49	2.22	1.49	0.98	0.51
440	4.44	2.27	1.51	1.00	0.52
450	4.38	2.31	1.54	1.01	0.53
460	4.31	2.33	1.55	1.03	0.54
470	4.25	2.38	1.59	1.04	0.54
480	4.20	2.41	1.61	1.05	0.55
490	4.13	2.45	1.63	1.07	0.56
500	4.07	2.48	1.66	1.08	0.57

Test 3
Initial Conditions
Reactor Temperature: 22.3°C
Reactor Pressure: 768.4 mm
Acetaldehyde Pressure: 126.6 mm
Nitrogen Dioxide Pressure: 0.02295 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	12.47	0.	0.	0.	0.
10	12.05	0.25	0.17	0.12	0.05
20	11.64	0.49	0.33	0.23	0.11
30	11.24	0.74	0.49	0.33	0.16
40	10.86	0.97	0.66	0.44	0.21
50	10.49	1.19	0.79	0.54	0.26
60	10.12	1.40	0.94	0.63	0.30
70	9.79	1.61	1.07	0.72	0.35
80	9.45	1.80	1.21	0.81	0.39
90	9.12	1.99	1.34	0.90	0.44
100	8.83	2.18	1.45	0.98	0.48
110	8.52	2.36	1.57	1.06	0.52
120	8.23	2.54	1.70	1.13	0.56
130	7.96	2.71	1.79	1.20	0.60
140	7.68	2.87	1.92	1.27	0.64
150	7.42	3.02	2.01	1.34	0.68
160	7.17	3.18	2.12	1.40	0.72
170	6.91	3.34	2.23	1.46	0.75
180	6.69	3.46	2.31	1.52	0.79
190	6.46	3.61	2.40	1.58	0.82
200	6.24	3.74	2.49	1.63	0.86
210	6.03	3.87	2.58	1.69	0.89
220	5.81	4.00	2.67	1.74	0.92
230	5.62	4.11	2.75	1.78	0.96
240	5.42	4.22	2.82	1.83	0.99
250	5.25	4.33	2.90	1.87	1.02
260	5.07	4.44	2.95	1.91	1.05
270	4.90	4.54	3.04	1.95	1.08
280	4.74	4.64	3.10	1.99	1.10
290	4.57	4.74	3.15	2.03	1.13
300	4.41	4.83	3.22	2.07	1.16

Test 3, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	4.25	4.93	3.28	2.10	1.18
320	4.17	5.00	3.34	2.13	1.21
330	3.98	5.10	3.40	2.16	1.24
340	3.83	5.18	3.44	2.19	1.26
350	3.71	5.26	3.50	2.22	1.28
360	3.58	5.32	3.55	2.25	1.31
370	3.46	5.40	3.60	2.27	1.33
380	3.34	5.48	3.65	2.30	1.35
390	3.22	5.54	3.70	2.32	1.38
400	3.12	5.61	3.74	2.34	1.40
410	3.01	5.67	3.78	2.36	1.42
420	2.91	5.74	3.82	2.38	1.44
430	2.81	5.79	3.86	2.40	1.46
440	2.72	5.85	3.90	2.42	1.48
450	2.62	5.91	3.94	2.44	1.50
460	2.54	5.95	3.97	2.46	1.51
470	2.45	6.01	4.01	2.47	1.54
480	2.37	6.06	4.04	2.49	1.55
490	2.28	6.11	4.07	2.50	1.57
500	2.21	6.16	4.11	2.52	1.59

Test 4
Initial Conditions
Reactor Temperature: 21.9°C
Reactor Pressure: 760.9 mm
Acetaldehyde Pressure: 123.3 mm
Nitrogen Dioxide Pressure: 0.01800 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	9.78	0.	0.	0.	0.
10	9.45	0.20	0.13	0.09	0.04
20	9.12	0.39	0.26	0.18	0.08
30	8.81	0.57	0.39	0.26	0.12
40	8.51	0.76	0.51	0.34	0.16
50	8.22	0.93	0.62	0.42	0.20
60	7.94	1.10	0.74	0.48	0.24
70	7.68	1.26	0.84	0.57	0.27
80	7.42	1.42	0.95	0.64	0.31
90	7.16	1.57	1.05	0.70	0.34
100	6.91	1.71	1.15	0.77	0.38
110	6.68	1.85	1.23	0.83	0.41
120	6.46	2.00	1.33	0.89	0.44
130	6.24	2.12	1.41	0.95	0.47
140	6.02	2.26	1.51	1.00	0.51
150	5.81	2.37	1.59	1.05	0.54
160	5.61	2.51	1.67	1.10	0.56
170	5.42	2.61	1.74	1.15	0.59
180	5.24	2.73	1.82	1.20	0.62
190	5.07	2.83	1.89	1.24	0.65
200	4.89	2.94	1.96	1.28	0.67
210	4.73	3.04	2.02	1.32	0.70
220	4.56	3.13	2.09	1.36	0.73
230	4.40	3.24	2.14	1.40	0.75
240	4.27	3.31	2.21	1.43	0.77
250	4.11	3.40	2.27	1.47	0.80
260	3.98	3.48	2.32	1.50	0.82
270	3.83	3.58	2.38	1.53	0.84
280	3.70	3.65	2.42	1.56	0.87
290	3.58	3.72	2.47	1.59	0.89
300	3.46	3.80	2.52	1.62	0.91

Test 4, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	3.34	3.89	2.58	1.65	0.93
320	3.22	3.93	2.62	1.67	0.95
330	3.11	3.99	2.67	1.70	0.97
340	3.01	4.06	2.73	1.72	0.99
350	2.90	4.13	2.74	1.74	1.01
360	2.80	4.19	2.78	1.76	1.03
370	2.72	4.24	2.84	1.78	1.04
380	2.62	4.30	2.87	1.80	1.06
390	2.53	4.35	2.89	1.82	1.08
400	2.43	4.40	2.94	1.84	1.10
410	2.37	4.45	2.98	1.86	1.12
420	2.28	4.49	2.99	1.87	1.13
430	2.20	4.55	3.03	1.87	1.15
440	2.13	4.59	3.05	1.90	1.16
450	2.05	4.64	3.08	1.92	1.18
460	1.98	4.68	3.13	1.93	1.19
470	1.92	4.73	3.15	1.94	1.21
480	1.86	4.77	3.17	1.95	1.22
490	1.79	4.80	3.20	1.96	1.23
500	1.73	4.83	3.22	1.98	1.25

Test 5
Initial Conditions
Reactor Temperature: 22.4°C
Reactor Pressure: 765.6 mm
Acetaldehyde Pressure: 35.5 mm
Nitrogen Dioxide Pressure: 0.01971 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	10.71	0.	0.	0.	0.
10	10.60	0.06	0.04	0.03	0.01
20	10.50	0.13	0.09	0.06	0.03
30	10.39	0.19	0.13	0.09	0.04
40	10.29	0.25	0.17	0.12	0.06
50	10.18	0.32	0.21	0.14	0.07
60	10.08	0.38	0.25	0.17	0.08
70	9.97	0.44	0.28	0.20	0.09
80	9.88	0.50	0.32	0.23	0.11
90	9.78	0.56	0.37	0.25	0.12
100	9.68	0.62	0.41	0.28	0.13
110	9.58	0.67	0.45	0.31	0.14
120	9.48	0.73	0.49	0.33	0.16
130	9.40	0.79	0.53	0.36	0.17
140	9.29	0.84	0.56	0.38	0.18
150	9.22	0.90	0.59	0.41	0.19
160	9.12	0.96	0.64	0.43	0.21
170	9.03	1.01	0.67	0.46	0.22
180	8.93	1.07	0.71	0.48	0.23
190	8.85	1.12	0.75	0.50	0.24
200	8.76	1.17	0.78	0.53	0.25
210	8.67	1.22	0.82	0.55	0.26
220	8.57	1.28	0.86	0.57	0.28
230	8.49	1.33	0.89	0.60	0.29
240	8.40	1.39	0.93	0.62	0.30
250	8.33	1.42	0.95	0.64	0.31
260	8.24	1.48	0.99	0.66	0.32
270	8.15	1.54	1.02	0.69	0.33
280	8.09	1.59	1.05	0.71	0.34
290	8.00	1.63	1.08	0.73	0.36
300	7.92	1.68	1.12	0.75	0.37

Test 5, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	7.85	1.72	1.16	0.77	0.38
320	7.76	1.77	1.18	0.79	0.39
330	7.68	1.82	1.20	0.81	0.40
340	7.61	1.86	1.23	0.83	0.41
350	7.53	1.91	1.27	0.85	0.42
360	7.45	1.95	1.30	0.87	0.43
370	7.39	2.01	1.33	0.89	0.44
380	7.31	2.04	1.35	0.91	0.45
390	7.22	2.09	1.38	0.93	0.46
400	7.17	2.12	1.41	0.95	0.47
410	7.09	2.17	1.46	0.97	0.48
420	7.02	2.22	1.48	0.98	0.49
430	6.95	2.26	1.51	1.00	0.50
440	6.88	2.31	1.53	1.02	0.51
450	6.81	2.33	1.56	1.04	0.52
460	6.75	2.37	1.60	1.06	0.53
470	6.67	2.42	1.62	1.07	0.54
480	6.61	2.46	1.63	1.09	0.55
490	6.55	2.50	1.68	1.11	0.56
500	6.47	2.54	1.69	1.12	0.57

Test 6
Initial Conditions
Reactor Temperature: 22.0°C
Reactor Pressure: 755.5 mm
Acetaldehyde Pressure: 146.9 mm
Nitrogen Dioxide Pressure: 0.01474 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	8.01	0.	0.	0.	0.
10	7.69	0.19	0.13	0.09	0.04
20	7.38	0.37	0.25	0.17	0.08
30	7.08	0.55	0.36	0.25	0.12
40	6.80	0.72	0.48	0.33	0.16
50	6.53	0.88	0.59	0.40	0.19
60	6.27	1.04	0.70	0.47	0.23
70	6.03	1.19	0.80	0.54	0.26
80	5.79	1.35	0.89	0.60	0.29
90	5.55	1.48	0.99	0.70	0.35
100	5.33	1.61	1.07	0.72	0.36
110	5.10	1.75	1.17	0.77	0.39
120	4.91	1.85	1.23	0.82	0.42
130	4.70	1.99	1.33	0.87	0.45
140	4.52	2.09	1.39	0.92	0.47
150	4.33	2.19	1.47	0.97	0.50
160	4.18	2.31	1.54	1.01	0.53
170	3.99	2.41	1.60	1.05	0.55
180	3.83	2.49	1.67	1.09	0.58
190	3.69	2.59	1.73	1.13	0.60
200	3.54	2.68	1.79	1.16	0.63
210	3.41	2.76	1.84	1.20	0.65
220	3.26	2.86	1.91	1.23	0.67
230	3.12	2.92	1.94	1.26	0.69
240	3.01	3.00	2.00	1.29	0.71
250	2.89	3.07	2.06	1.31	0.73
260	2.76	3.14	2.10	1.34	0.75
270	2.65	3.20	2.13	1.37	0.77
280	2.55	3.27	2.18	1.39	0.79
290	2.44	3.34	2.22	1.41	0.81
300	2.35	3.39	2.26	1.43	0.83

Test 6, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	2.27	3.44	2.30	1.45	0.85
320	2.18	3.50	2.34	1.47	0.87
330	2.08	3.56	2.36	1.49	0.88
340	2.01	3.61	2.40	1.51	0.90
350	1.93	3.65	2.44	1.52	0.91
360	1.83	3.69	2.46	1.54	0.93
370	1.78	3.75	2.50	1.55	0.94
380	1.70	3.79	2.53	1.57	0.96
390	1.64	3.84	2.55	1.58	0.97
400	1.56	3.87	2.58	1.59	0.99
410	1.49	3.90	2.60	1.60	1.00
420	1.43	3.93	2.63	1.61	1.01
430	1.38	3.98	2.64	1.62	1.03
440	1.34	3.99	2.67	1.63	1.04
450	1.28	4.03	2.69	1.64	1.05
460	1.22	4.06	2.71	1.65	1.07
470	1.18	4.10	2.73	1.66	1.08
480	1.13	4.14	2.75	1.67	1.09
490	1.08	4.16	2.77	1.67	1.10
500	1.04	4.18	2.79	1.68	1.11

Test 7
Initial Conditions
Reactor Temperature: 21.7°C
Reactor Pressure: 775.1 mm
Acetaldehyde Pressure: 22.8 mm
Nitrogen Dioxide Pressure: 0.01856 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	10.08	0.	0.	0.	0.
10	10.01	0.04	0.03	0.02	0.01
20	9.96	0.08	0.05	0.04	0.02
30	9.88	0.12	0.08	0.05	0.02
40	9.83	0.16	0.10	0.07	0.03
50	9.76	0.20	0.13	0.09	0.04
60	9.68	0.23	0.16	0.11	0.05
70	9.63	0.27	0.18	0.12	0.06
80	9.57	0.31	0.21	0.14	0.07
90	9.50	0.36	0.23	0.16	0.08
100	9.43	0.38	0.26	0.17	0.08
110	9.39	0.42	0.28	0.19	0.09
120	9.32	0.46	0.30	0.21	0.10
130	9.27	0.49	0.33	0.22	0.10
140	9.20	0.53	0.35	0.24	0.11
150	9.14	0.57	0.38	0.26	0.12
160	9.08	0.60	0.40	0.27	0.13
170	9.03	0.64	0.42	0.29	0.14
180	8.96	0.67	0.45	0.30	0.14
190	8.89	0.71	0.47	0.32	0.15
200	8.84	0.74	0.49	0.33	0.16
210	8.79	0.78	0.52	0.35	0.17
220	8.74	0.81	0.54	0.37	0.17
230	8.65	0.85	0.56	0.38	0.18
240	8.62	0.88	0.59	0.40	0.19
250	8.56	0.91	0.61	0.41	0.20
260	8.50	0.95	0.63	0.43	0.20
270	8.45	0.98	0.65	0.44	0.21
280	8.39	1.01	0.68	0.46	0.22
290	8.34	1.05	0.70	0.47	0.23
300	8.28	1.08	0.72	0.49	0.23

Test 7, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	8.24	1.10	0.74	0.50	0.24
320	8.18	1.14	0.76	0.51	0.25
330	8.12	1.17	0.78	0.53	0.25
340	8.08	1.21	0.80	0.54	0.26
350	8.02	1.24	0.83	0.56	0.27
360	7.96	1.27	0.85	0.57	0.28
370	7.91	1.30	0.87	0.58	0.28
380	7.85	1.32	0.89	0.60	0.29
390	7.80	1.36	0.91	0.61	0.30
400	7.77	1.39	0.93	0.63	0.30
410	7.71	1.42	0.95	0.64	0.31
420	7.66	1.45	0.97	0.65	0.32
430	7.61	1.48	0.99	0.67	0.33
440	7.57	1.51	1.01	0.68	0.33
450	7.51	1.54	1.04	0.69	0.34
460	7.47	1.56	1.05	0.70	0.34
470	7.41	1.60	1.07	0.72	0.35
480	7.36	1.62	1.09	0.73	0.36
490	7.31	1.67	1.11	0.74	0.36
500	7.27	1.69	1.13	0.76	0.37

Test 8
Initial Conditions
Reactor Temperature: 22.0°C
Reactor Pressure: 759.0 mm
Acetaldehyde Pressure: 51.6 mm
Nitrogen Dioxide Pressure: 0.01246 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	6.77	0.	0.	0.	0.
10	6.66	0.06	0.04	0.03	0.01
20	6.57	0.12	0.08	0.05	0.02
30	6.48	0.18	0.12	0.08	0.04
40	6.38	0.23	0.15	0.11	0.05
50	6.30	0.29	0.19	0.13	0.06
60	6.20	0.34	0.23	0.16	0.07
70	6.11	0.40	0.27	0.18	0.08
80	6.02	0.45	0.30	0.20	0.10
90	5.94	0.50	0.34	0.23	0.11
100	5.84	0.56	0.37	0.25	0.12
110	5.76	0.61	0.41	0.27	0.13
120	5.67	0.66	0.44	0.30	0.14
130	5.58	0.71	0.47	0.32	0.15
140	5.52	0.76	0.50	0.34	0.16
150	5.43	0.81	0.54	0.36	0.17
160	5.36	0.85	0.57	0.38	0.18
170	5.26	0.90	0.60	0.40	0.20
180	5.19	0.95	0.63	0.43	0.21
190	5.12	0.99	0.66	0.44	0.22
200	5.04	1.04	0.69	0.46	0.23
210	4.98	1.07	0.72	0.48	0.24
220	4.89	1.12	0.75	0.50	0.25
230	4.82	1.17	0.78	0.52	0.26
240	4.75	1.22	0.81	0.54	0.27
250	4.68	1.24	0.84	0.56	0.28
260	4.62	1.29	0.85	0.58	0.29
270	4.56	1.33	0.89	0.59	0.29
280	4.47	1.37	0.92	0.61	0.30
290	4.42	1.41	0.94	0.63	0.31
300	4.35	1.45	0.97	0.64	0.32

Test 8, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	4.30	1.50	0.99	0.66	0.33
320	4.23	1.53	1.02	0.68	0.34
330	4.16	1.56	1.04	0.69	0.35
340	4.10	1.59	1.07	0.71	0.36
350	4.04	1.64	1.08	0.72	0.37
360	3.98	1.66	1.11	0.74	0.38
370	3.93	1.71	1.14	0.76	0.38
380	3.88	1.73	1.15	0.77	0.39
390	3.81	1.78	1.18	0.78	0.40
400	3.76	1.82	1.21	0.80	0.41
410	3.69	1.83	1.23	0.81	0.42
420	3.65	1.87	1.26	0.82	0.43
430	3.59	1.91	1.26	0.84	0.43
440	3.53	1.94	1.28	0.85	0.44
450	3.49	1.98	1.31	0.86	0.45
460	3.45	2.01	1.33	0.87	0.46
470	3.39	2.03	1.35	0.89	0.47
480	3.35	2.07	1.37	0.90	0.47
490	3.29	2.09	1.39	0.91	0.48
500	3.24	2.12	1.41	0.92	0.49

Test 9
Initial Conditions
Reactor Temperature: 22.0°C
Reactor Pressure: 771.8 mm
Acetaldehyde Pressure: 130.0 mm
Nitrogen Dioxide Pressure: 0.01219 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	6.62	0.	0.	0.	0.
10	6.38	0.14	0.09	0.06	0.03
20	6.15	0.27	0.18	0.13	0.06
30	5.93	0.41	0.27	0.19	0.09
40	5.72	0.53	0.35	0.24	0.12
50	5.52	0.65	0.43	0.30	0.14
60	5.32	0.77	0.51	0.35	0.17
70	5.13	0;89	0.59	0.40	0.19
80	4.94	1.00	0.66	0.45	0.22
90	4.77	1.10	0.73	0.50	0.24
100	4.60	1.21	0.80	0.54	0.27
110	4.43	1.30	0.87	0.58	0.30
120	4.28	1.40	0.93	0.62	0.31
130	4.12	1.49	0.99	0.66	0.33
140	3.98	1.58	1.05	0.70	0.36
150	3.83	1.66	1.11	0.74	0.38
160	3.70	1.75	1.16	0.77	0.40
170	3.56	1.83	1.22	0.80	0.42
180	3.44	1.90	1.27	0.84	0.44
190	3.31	1.98	1.32	0.87	0.45
200	3.20	2.05	1.36	0.89	0.47
210	3.08	2.12	1.41	0.92	0.49
220	2.97	2.18	1.45	0.85	0.51
230	2.86	2.25	1.50	0.97	0.53
240	2.76	2.31	1.54	1.00	0.54
250	2.66	2.37	1.58	1.02	0.56
260	2.57	2.42	1.61	1.04	0.58
270	2.48	2.48	1.65	1.06	0.59
280	2.39	2.53	1.69	1.08	0.61
290	2.30	2.58	1.72	1.10	0.62
300	2.22	2.63	1.75	1.12	0.64

Test 9, continued

Time (min)	NO_2	Concentration (10^{-7} moles/liter) NO	CO_2	CH_3ONO	CH_3NO_2
310	2.14	2.68	1.78	1.14	0.65
320	2.06	2.73	1.82	1.16	0.66
330	1.99	2.77	1.84	1.17	0.68
340	1.92	2.81	1.87	1.19	0.69
350	1.85	2.85	1.90	1.20	0.70
360	1.78	2.89	1.93	1.21	0.72
370	1.72	2.93	1.95	1.23	0.73
380	1.66	2.97	1.98	1.24	0.74
390	1.60	3.00	2.00	1.25	0.75
400	1.54	3.04	2.02	1.26	0.76
410	1.49	3.07	2.05	1.28	0.77
420	1.43	3.10	2.07	1.29	0.79
430	1.38	3.13	2.09	1.30	0.80
440	1.33	3.16	2.11	1.31	0.81
450	1.29	3.19	2.13	1.31	0.82
460	1.24	3.22	2.15	1.32	0.83
470	1.19	3.25	2.16	1.33	0.84
480	1.15	3.27	2.18	1.34	0.85
490	1.11	3.30	2.20	1.35	0.86
500	1.07	3.32	2.21	1.35	0.86

Test 10
Initial Conditions
Reactor Temperature: 22.0°C
Reactor Pressure: 752.8 mm
Acetaldehyde Pressure: 146.7 mm
Nitrogen Dioxide Pressure: 0.01285 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	6.98	0.	0.	0.	0.
10	6.70	0.17	0.11	0.08	0.03
20	6.45	0.32	0.22	0.15	0.07
30	6.18	0.48	0.32	0.22	0.11
40	5.93	0.62	0.42	0.28	0.13
50	5.71	0.76	0.52	0.34	0.17
60	5.47	0.89	0.60	0.40	0.20
70	5.26	1.02	0.69	0.46	0.22
80	5.06	1.15	0.78	0.52	0.25
90	4.86	1.27	0.86	0.57	0.28
100	4.66	1.40	0.93	0.62	0.31
110	4.49	1.49	1.00	0.67	0.33
120	4.30	1.61	1.06	0.71	0.36
130	4.13	1.71	1.15	0.75	0.38
140	3.98	1.81	1.20	0.80	0.41
150	3.81	1.89	1.27	0.84	0.43
160	3.65	1.98	1.33	0.87	0.45
170	3.52	2.09	1.39	0.91	0.48
180	3.38	2.15	1.43	0.94	0.50
190	3.24	2.23	1.49	0.97	0.52
200	3.12	2.33	1.55	1.01	0.54
210	2.99	2.39	1.59	1.03	0.56
220	2.87	2.46	1.64	1.06	0.58
230	2.75	2.55	1.69	1.10	0.60
240	2.64	2.60	1.72	1.11	0.62
250	2.55	2.67	1.77	1.14	0.63
260	2.45	2.71	1.81	1.16	0.65
270	2.36	2.79	1.85	1.18	0.67
280	2.26	2.83	1.89	1.20	0.69
290	2.17	2.89	1.93	1.22	0.70
300	2.08	2.95	1.97	1.24	0.72

Test 10, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	2.01	3.00	1.99	1.26	0.73
320	1.91	3.04	2.02	1.28	0.75
330	1.84	3.08	2.05	1.29	0.76
340	1.76	3.12	2.08	1.31	0.78
350	1.69	3.17	2.10	1.32	0.79
360	1.63	3.21	2.15	1.33	0.80
370	1.58	3.25	2.16	1.35	0.82
380	1.51	3.28	2.20	1.36	0.83
390	1.45	3.33	2.21	1.37	0.84
400	1.38	3.35	2.24	1.38	0.85
410	1.34	3.39	2.26	1.39	0.87
420	1.28	3.43	2.29	1.40	0.88
430	1.23	3.46	2.31	1.41	0.89
440	1.18	3.48	2.33	1.42	0.90
450	1.14	3.51	2.33	1.43	0.91
460	1.09	3.53	2.36	1.43	0.92
470	1.06	3.57	2.37	1.44	0.93
480	1.01	3.58	2.40	1.45	0.94
490	0.97	3.61	2.40	1.45	0.95
500	0.93	3.63	2.42	1.46	0.96

Test 11
Initial Conditions
Reactor Temperature: 22.0°C
Reactor Pressure: 772.2 mm
Acetaldehyde Pressure: 77.1 mm
Nitrogen Dioxide Pressure: 0.01554 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	8.44	0.	0.	0.	0.
10	8.26	0.11	0.07	0.05	0.02
20	8.08	0.22	0.15	0.10	0.05
30	7.89	0.32	0.22	0.15	0.07
40	7.73	0.43	0.28	0.19	0.09
50	7.56	0.53	0.34	0.24	0.11
60	7.40	0.63	0.42	0.28	0.13
70	7.24	0.71	0.47	0.33	0.15
80	7.08	0.82	0.54	0.37	0.18
90	6.93	0.91	0.61	0.41	0.20
100	6.78	1.00	0.67	0.45	0.22
110	6.64	1.09	0.72	0.49	0.24
120	6.49	1.17	0.77	0.53	0.26
130	6.34	1.26	0.84	0.56	0.27
140	6.21	1.33	0.89	0.60	0.29
150	6.06	1.41	0.95	0.94	0.31
160	5.95	1.49	0.99	0.68	0.33
170	5.81	1.58	1.05	0.70	0.35
180	5.68	1.65	1.10	0.74	0.37
190	5.55	1.72	1.15	0.77	0.38
200	5.44	1.80	1.20	0.80	0.40
210	5.32	1.86	1.24	0.83	0.42
220	5.21	1.93	1.29	0.86	0.43
230	5.09	2.01	1.34	0.89	0.45
240	4.98	2.07	1.38	0.92	0.47
250	4.87	2.15	1.43	0.94	0.48
260	4.78	2.20	1.48	0.97	0.50
270	4.67	2.26	1.52	1.00	0.51
280	4.56	2.33	1.54	1.02	0.53
290	4.46	2.39	1.58	1.05	0.54
300	4.37	2.44	1.84	1.07	0.56

Test 11, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	4.27	2,49	1.67	1.09	0.57
320	4.17	2.56	1.70	1.12	0.59
330	4.09	2.61	1.74	1.14	0.60
340	4.00	2.66	1.78	1.16	0.62
350	3.91	2.72	1.80	1.18	0.63
360	3.83	2.77	1.84	1.20	0.64
370	3.75	2.82	1.88	1.22	0.66
380	3.66	2.87	1.91	1.24	0.67
390	3.58	2.91	1.94	1.26	0.68
400	3.51	2.96	1.97	1.28	0.70
410	3.42	2.99	1.99	1.30	0.71
420	3.36	3.05	2.03	1.31	0.72
430	3.28	3.09	2.06	1.33	0.73
440	3.21	3.14	2.08	1.35	0.75
450	3.14	3.19	2.13	1.36	0.76
460	3.07	3.22	2.15	1.38	0.77
470	3.01	3.26	2.17	1.39	0.78
480	2.93	3.31	2.21	1.41	0.79
490	2.89	3.34	2.22	1.42	0.80
500	2.82	3.37	2.25	1.44	0.81

Test 12
Initial Conditions
Reactor Temperature: 21.8°C
Reactor Pressure: 768.1 mm
Acetaldehyde Pressure: 80.3 mm
Nitrogen Dioxide Pressure: 0.01165 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	6.33	0.	0.	0.	0.
10	6.19	0.09	0.06	0.04	0.02
20	6.04	0.17	0.11	0.08	0.04
30	5.91	0.25	0.17	0.12	0.05
40	5.76	0.34	0.22	0.15	0.07
50	5.64	0.41	0.28	0.19	0.08
60	5.50	0.49	0.33	0.22	0.11
70	5.38	0.57	0.38	0.26	0.12
80	5.25	0.63	0.43	0.29	0.14
90	5.13	0.71	0.48	0.32	0.15
100	5.02	0.78	0.52	0.35	0.17
110	4.92	0.85	0.57	0.38	0.18
120	4.80	0.92	0.61	0.41	0.20
130	4.69	0.99	0.66	0.44	0.22
140	4.59	1.04	0.69	0.47	0.23
150	4.48	1.11	0.74	0.50	0.24
160	4.37	1.17	0.78	0.52	0.26
170	4.27	1.23	0.82	0.55	0.27
180	4.18	1.29	0.85	0.56	0.29
190	4.09	1.34	0.89	0.60	0.30
200	3.99	1.41	0.94	0.62	0.31
210	3.90	1.46	0.97	0.65	0.33
220	3.81	1.51	1.01	0.67	0.34
230	3.73	1.57	1.04	0.69	0.35
240	3.63	1.62	1.08	0.71	0.37
250	3.54	1.67	1.10	0.73	0.38
260	3.47	1.72	1.14	0.75	0.40
270	3.38	1.76	1.18	0.77	0.40
280	3.31	1.82	1.21	0.79	0.41
290	3.24	1.86	1.24	0.81	0.42
300	3.16	1.91	1.27	0.83	0.44

Test 12, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	3.09	1.94	1.30	0.85	0.45
320	3.01	1.99	1.32	0.86	0.46
330	2.95	2.03	1.34	0.88	0.47
340	2.88	2.07	1.38	0.90	0.48
350	2.83	2.11	1.40	0.91	0.49
360	2.75	2.16	1.42	0.93	0.50
370	2.69	2.18	1.46	0.94	0.51
380	2.64	2.22	1.47	0.96	0.52
390	2.57	2.26	1.50	0.97	0.53
400	2.50	2.28	1.53	0.99	0.54
410	2.45	2.33	1.54	1.00	0.55
420	2.40	2.37	1.57	1.01	0.56
430	2.34	2.39	1.59	1.03	0.57
440	2.30	2.42	1.62	1.04	0.60
450	2.24	2.46	1.64	1.05	0.59
460	2.19	2.49	1.66	1.06	0.60
470	2.14	2.52	1.68	1.07	0.61
480	2.09	2.55	1.70	1.08	0.61
490	2.05	2.57	1.72	1.09	0.62
500	1.99	2.60	1.73	1.10	0.63

Test 13
Initial Conditions
Reactor Temperature: 21.9°C
Reactor Pressure: 753.6 mm
Acetaldehyde Pressure: 86.5 mm
Nitrogen Dioxide Pressure: 0.01382 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	7.51	0.	0.	0.	0.
10	7.33	0.11	0.07	0.05	0.02
20	7.15	0.22	0.15	0.10	0.05
30	6.97	0.32	0.22	0.15	0.07
40	6.70	0.43	0.28	0.19	0.09
50	6.64	0.52	0.35	0.24	0.11
60	6.47	0.62	0.41	0.28	0.13
70	6.31	0.72	0.48	0.32	0.15
80	6.17	0.80	0.53	0.34	0.17
90	6.00	0.90	0.60	0.41	0.19
100	5.86	0.99	0.66	0.44	0.21
110	5.73	1.07	0.72	0.48	0.23
120	5.58	1.16	0.77	0.52	0.25
130	5.44	1.24	0.83	0.56	0.27
140	5.32	1.31	0.87	0.59	0.29
150	5.18	1.40	0.93	0.62	0.31
160	5.05	1.47	0.98	0.66	0.33
170	4.94	1.56	1.03	0.69	0.34
180	4.82	1.61	1.07	0.72	0.36
190	4.69	1.69	1.13	0.75	0.38
200	4.58	1.75	1.18	0.78	0.39
210	4.46	1.83	1.22	0.81	0.41
220	4.35	1.89	1.26	0.84	0.43
230	4.25	1.96	1.30	0.86	0.44
240	4.14	2.03	1.35	0.89	0.46
250	4.04	2.07	1.39	0.91	0.47
260	3.94	2.15	1.43	0.94	0.49
270	3.85	2.20	1.47	0.96	0.50
280	3.75	2.25	1.50	0.99	0.52
290	3.65	2.32	1.55	1.01	0.53
300	3.57	2.36	1.58	1.03	0.55

Test 13, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	3.48	2.42	1.60	1.05	0.56
320	3.41	2.47	1.64	1.07	0.57
330	3.32	2.52	1.68	1.09	0.59
340	3.23	2.57	1.70	1.11	0.60
350	3.16	2.61	1.73	1.13	0.61
360	3.09	2.67	1.77	1.15	0.63
370	3.00	2.70	1.80	1.16	0.64
380	2.94	2.76	1.83	1.18	0.65
390	2.86	2.78	1.85	1.20	0.66
400	2.79	2.83	1.89	1.21	0.67
410	2.72	2.87	1.92	1.23	0.69
420	2.65	2.91	1.94	1.24	0.70
430	2.59	2.95	1.97	1.26	0.71
440	2.52	2.98	1.99	1.27	0.72
450	2.46	3.04	2.03	1.29	0.73
460	2.40	3.06	2.04	1.30	0.74
470	2.34	3.06	2.04	1.30	0.74
480	2.29	3.13	2.10	1.33	0.76
490	2.22	3.17	2.10	1.34	0.77
500	2.18	3.20	2.13	1.35	0.78

Test 14
Initial Conditions
Reactor Temperature: 22.0°C
Reactor Pressure: 760.8 mm
Acetaldehyde Pressure: 56.9 mm
Nitrogen Dioxide Pressure: 0.01732 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	9.41	0.	0.	0.	0.
10	9.26.	0.09	0.06	0.04	0.02
20	9.11	0.17	0.12	0.08	0.04
30	8.97	0.26	0.17	0.12	0.05
40	8.84	0.34	0.23	0.16	0.07
50	8.70	0.42	0.28	0.19	0.09
60	8.58	0.50	0.34	0.23	0.11
70	8.44	5.84	0.39	0.26	0.12
80	8.31	0.66	0.44	0.30	0.14
90	8.19	0.74	0.49	0.33	0.16
100	8.05	0.81	0.54	0.37	0.17
110	7.92	0.89	0.59	0.40	0.19
120	7.80	0.96	0.64	0.43	0.21
130	7.68	1.04	0.69	0.47	0.22
140	7.57	1.11	0.74	0.50	0.24
150	7.45	1.18	0.78	0.53	0.26
160	7.33	1.25	0.82	0.56	0.27
170	7.23	1.31	0.88	0.59	0.29
180	7.11	1.38	0.92	0.62	0.30
190	7.00	1.45	0.96	0.65	0.32
200	6.89	1.51	1.01	0.68	0.33
210	6.78	1.58	1.05	0.71	0.35
220	6.68	1.64	1.09	0.73	0.36
230	6.58	1.69	1.13	0.76	0.37
240	6.47	1.76	1.17	0.79	0.39
250	6.37	1.82	1.21	0.81	0.40
260	6.27	1.87	1.25	0.84	0.42
270	6.18	1.95	1.29	0.86	0.43
280	6.08	2.00	1.33	0.89	0.44
290	6.00	2.05	1.38	0.91	0.46
300	5.90	2.11	1.41	0.94	0.47

Test 14, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	5.80	2.16	1.44	0.96	0.48
320	5.71	2.22	1.48	0.98	0.50
330	5.63	2.26	1.51	1.00	0.51
340	5.55	2.32	1.56	1.03	0.52
350	5.45	2.37	1.58	1.05	0.54
360	5.38	2.42	1.62	1.07	0.55
370	5.29	2.47	1.66	1.09	0.56
380	5.20	2.52	1.68	1.11	0.57
390	5.12	2.56	1.71	1.13	0.58
400	5.04	2.63	1.75	1.15	0.60
410	4.97	2.67	1.78	1.17	0.61
420	4.90	2.71	1.81	1.19	0.62
430	4.81	2.76	1.85	1.21	0.63
440	4.75	2.81	1.88	1.23	0.64
450	4.67	2.85	1.90	1.24	0.65
460	4.59	2.90	1.93	1.26	0.67
470	4.52	2.93	1.95	1.28	0.68
480	4.45	2.97	1.98	1.30	0.69
490	4.38	3.02	2.01	1.31	0.70
500	4.32	3.06	2.04	1.33	0.71

Test 15
Initial Conditions
Reactor Temperature: 22.6°C
Reactor Pressure: 757.8 mm
Acetaldehyde Pressure: 104.6 mm
Nitrogen Dioxide Pressure: 0 .01436

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	7.80	0.	0.	0.	0.
10	7.57	0.14	0.09	0.06	0.03
20	7.34	0.27	0.18	0.12	0.06
30	7.14	0.40	0.27	0.18	0.08
40	6.93	0.52	0.35	0.24	0.11
50	6.72	0.65	0.43	0.29	0.14
60	6.53	0.76	0.51	0.35	0.16
70	6.34	0.88	0.59	0.40	0.19
80	6.14	0.99	0.66	0.45	0.21
90	5.96	1.10	0.73	0.49	0.24
100	5.80	1.20	0.80	0.54	0.26
110	5.63	1.30	0.87	0.58	0.28
120	5.45	1.40	0.94	0.63	0.31
130	5.29	1.51	1.00	0.67	0.34
140	5.15	1.59	1.05	0.71	0.35
150	5.00	1.68	1.11	0.75	0.37
160	4.86	1.76	1.17	0.78	0.40
170	4.71	1.86	1.24	0.82	0.42
180	4.58	1.95	1.29	0.86	0.44
190	4.44	2.03	1.35	0.89	0.46
200	4.31	2.10	1.40	0.92	0.48
210	4.18	2.17	1.45	0.95	0.49
220	4.06	2.25	1.50	0.98	0.51
230	3.95	2.32	1.54	1.01	0.53
240	3.82	2.39	1.59	1.04	0.55
250	3.70	2.45	1.64	1.07	0.57
260	3.60	2.53	1.69	1.09	0.58
270	3.50	2.57	1.71	1.12	0.60
280	3.40	2.64	1.75	1.14	0.62
290	3.30	2.70	1.80	1.17	0.63
300	3.21	2.75	1.83	1.19	0.50

Test 15, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	3.11	2.82	1.88	1.21	0.67
320	3.01	2.86	1.91	1.23	0.68
330	2.93	2.92	1.96	1.25	0.70
340	2.83	2.98	1.98	1.27	0.71
350	2.76	3.03	2.02	1.29	0.72
360	2.68	3.07	2.06	1.31	0.74
370	2.61	3.11	2.07	1.33	0.75
380	2.52	3.17	2.10	1.34	0.77
390	2.46	3.20	2.13	1.36	0.78
400	2.38	3.25	2.18	1.38	0.79
410	2.31	3.30	2.20	1.39	0.81
420	2.23	3.34	2.22	1.41	0.82
430	2.17	3.38	2.24	1.42	0.83
440	2.10	3.41	2.28	1.43	0.84
450	2.06	3.44	2.29	1.45	0.85
460	2.00	3.49	2.32	1.46	0.87
470	1.93	3.52	2.35	1.47	0.88
480	1.87	3.56	2.36	1.48	0.89
490	1.83	3.60	2.39	1.49	0.90
500	1.77	3.62	2.41	1.50	0.91

Test 16
Initial Conditions
Reactor Temperature: 22.3°C
Reactor Pressure: 762.7 mm
Acetaldehyde Pressure: 108.9 mm
Nitrogen Dioxide Pressure: 0.01272 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	6.91	0.	0.	0.	0.
10	6.71	0.12	0.08	0.06	0.03
20	6.50	0.24	0.16	0.11	0.05
30	6.32	0.35	0.24	0.16	0.08
40	6.14	0.47	0.31	0.21	0.10
50	5.96	0.58	0.38	0.26	0.12
60	5.78	0.68	0.45	0.31	0.15
70	5.61	0.78	0.52	0.35	0.17
80	5.46	0.88	0.58	0.39	0.19
90	5.28	0.96	0.65	0.44	0.21
100	5.14	1.06	0.71	0.48	0.23
110	4.99	1.15	0.78	0.52	0.25
120	4.84	1.24	0.83	0.55	0.27
130	4.70	1.32	0.88	0.59	0.29
140	4.55	1.42	0.94	0.63	0.31
150	4.43	1.50	0.99	0.66	0.33
160	4.30	1.57	1.04	0.69	0.35
170	4.17	1.64	1.10	0.73	0.37
180	4.03	1.72	1.14	0.76	0.39
190	3.93	1.79	1.19	0.79	0.40
200	3.82	1.86	1.24	0.82	0.42
210	3.71	1.93	1.27	0.84	0.44
220	3.60	1.99	1.33	0.87	0.45
230	3.48	2.05	1.37	0.90	0.47
240	3.39	2.11	1.41	0.92	0.47
250	3.28	2.16	1.45	0.95	0.50
260	3.19	2.23	1.49	0.97	0.52
270	3.09	2.29	1.52	0.99	0.53
280	3.01	2.35	1.57	1.01	0.55
290	2.92	2.39	1.60	1.03	0.56
300	2.84	2,44	1.64	1.05	0.58

Test 16, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	2.75	2.49	1.66	1.07	0.59
320	2.67	2.54	1.69	1.09	0.60
330	2.60	2.60	1.73	1.11	0.62
340	2.53	2.63	1.76	1.13	0.63
350	2.45	2.68	1.79	1.14	0.64
360	2.37	2.72	1.81	1.16	0.65
370	2.30	2.76	1.84	1.18	0.67
380	2.24	2.80	1.88	1.19	0.68
390	2.16	2.84	1.90	1.21	0.69
400	2.11	2.88	1.91	1.22	0.70
410	2.05	2.93	1.95	1.23	0.71
420	1.99	2.95	1.98	1.24	0.72
430	1.94	3.00	1.99	1.26	0.74
440	1.87	3.02	2.02	1.27	0.75
450	1.82	3.06	2.04	1.28	0.76
460	1.76	3.09	2.06	1.29	0.77
470	1.71	3.12	2.08	1.30	0.78
480	1.66	3.16	2.11	1.31	0.79
490	1.61	3.18	2.12	1.32	0.80
500	1.57	3.21	2.14	1.33	0.81

Test 17
Initial Conditions
Reactor Temperature: 21.9°C
Reactor Pressure: 768.6 mm
Acetaldehyde Pressure: 120.8 mm
Nitrogen Dioxide Pressure: 0.02358 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	12.81	0.	0.	0.	0.
10	12.38	0.26	0.17	0.12	0.05
20	11.97	0.51	0.34	0.23	0.11
30	11.57	0.75	0.50	0.34	0.16
40	11.18	0.98	0.53	0.44	0.21
50	10.79	1.20	0.80	0.54	0.26
60	10.44	1.41	0.95	0.64	0.31
70	10.09	1.62	1.09	0.73	0.35
80	9.75	1.83	1.22	0.82	0.40
90	9.43	2.04	1.36	0.91	0.44
100	9.10	2.23	1.49	0.99	0.49
110	8.81	2.40	1.59	1.07	0.53
120	8.50	2.59	1.73	1.15	0.57
130	8.23	2.74	1.83	1.22	0.61
140	7.94	2.92	1.94	1.29	0.65
150	7.68	3.08	2.04	1.36	0.69
160	7.43	3.24	2.15	1.43	0.73
170	7.19	3.39	2.25	1.49	0.77
180	6.94	3.52	2.36	1.55	0.80
190	6.71	3.66	2.43	1.61	0.84
200	6.47	3.80	2.52	1.66	0.87
210	6.26	3.93	2.63	1.71	0.90
220	6.05	4.05	2.70	1.77	0.94
230	5.84	4.18	2.78	1.81	0.97
240	5.65	4.29	2.86	1.86	1.00
250	5.47	4.41	2.94	1.91	1.03
260	5.28	4.52	3.00	1.95	1.06
270	5.11	4.62	3.07	1.99	1.09
280	4.93	4.73	3.14	2.03	1.12
290	4.78	4.82	3.22	2.07	1.15
300	4.62	4.91	3.27	2.10	1.18

Test 17, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	4.46	5.01	3.34	2.14	1.20
320	4.31	5.10	3.39	2.17	1.23
330	4.15	5.20	3.47	2.20	1.26
340	4.02	5.27	3.52	2.23	1.28
350	3.89	5.35	3.58	2.26	1.31
360	3.76	5.42	3.61	2.29	1.33
370	3.63	5.51	3.66	2.32	1.35
380	3.52	5.57	3.71	2.34	1.38
390	3.39	5.64	3.77	2.37	1.40
400	3.29	5.73	3.81	2.39	1.42
410	3.18	5.78	3.86	2.41	1.44
420	3.06	5.86	3.91	2.44	1.46
430	2.96	5.91	3.94	2.46	1.48
440	2.85	5.98	3.99	2.48	1.50
450	2.77	6.03	4.02	2.49	1.52
460	2.67	6.08	4.06	2.51	1.54
470	2.58	6.14	4.09	2.53	1.56
480	2.50	6.20	4.13	2.54	1.58
490	2.41	6.25	4.17	2.56	1.60
500	2.32	6.29	4.18	2.57	1.62

Test 18
Initial Conditions
Reactor Temperature: 22.0°C
Reactor Pressure: 608.7 mm
Acetaldehyde Pressure: 69.2 mm
Nitrogen Dioxide Pressure: 0.02196 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	11.93	0.	0.	0.	0.
10	11.70	0.13	0.09	0.06	0.02
20	11.47	0.27	0.18	0.12	0.05
30	11.25	0.40	0.26	0.18	0.08
40	11.04	0.53	0.35	0.24	0.11
50	10.82	0.66	0.44	0.30	0.14
60	10.62	0.78	0.52	0.35	0.16
70	10.41	0.90	0.60	0.41	0.19
80	10.21	1.02	0.68	0.46	0.22
90	10.01	1.14	0.76	0.51	0.24
100	9.82	1.26	0.84	0.56	0.27
110	9.63	1.37	0.91	0.61	0.29
120	9.45	1.48	0.99	0.66	0.32
130	9.27	1.59	1.06	0.71	0.34
140	9.09	1.70	1.13	0.76	0.37
150	8.91	1.80	1.20	0.81	0.39
160	8.74	1.90	1.27	0.85	0.41
170	8.57	2.01	1.34	0.89	0.44
180	8.41	2.10	1.40	0.94	0.46
190	8.25	2.20	1.47	0.98	0.48
200	8.09	2.30	1.53	1.02	0.51
210	7.93	2.39	1.59	1.06	0.53
220	7.78	2.48	1.65	1.10	0.55
230	7.63	2.57	1.71	1.14	0.57
240	7.49	2.66	1.77	1.18	0.59
250	7.34	2.75	1.83	1.21	0.61
260	7.20	2.83	1.89	1.25	0.63
270	7.06	2.91	1.94	1.28	0.65
280	6.93	2.99	1.99	1.32	0.67
290	6.79	3.07	2.05	1.35	0.69
300	6.66	3.15	2.10	1.38	0.71

Test 18, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	6.53	3.23	2.15	1.42	0.73
320	6.41	3.30	2.20	1.45	0.75
330	6.29	3.38	2.25	1.47	0.77
340	6.17	3.45	2.30	1.51	0.79
350	6.05	3.52	2.35	1.54	0.80
360	5.93	3.59	2.39	1.57	0.82
370	5.82	3.66	2.44	1.59	0.84
380	5.70	3.73	2.48	1.62	0.86
390	5.59	3.79	2.53	1.65	0.88
400	5.49	3.86	2.57	1.67	0.89
410	5.38	3.92	2.61	1.70	0.91
420	5.28	3.98	2.65	1.72	0.92
430	5.18	4.04	2.69	1.75	0.94
440	5.08	4.10	2.73	1.77	0.96
450	4.98	4.16	2.77	1.79	0.97
460	4.88	4.22	2.81	1.82	0.99
470	4.79	4.28	2.85	1.84	1.00
480	4.70	4.33	2.89	1.86	1.02
490	4.61	4.39	2.92	1.88	1.04
500	4.52	4.44	2.96	1.90	1.05

Test 19
Initial Conditions
Reactor Temperature: 22.2°C
Reactor Pressure: 516.6 mm
Acetaldehyde Pressure: 67.2 mm
Nitrogen Dioxide Pressure: 0.01194 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	6.50	0.	0.	0.	0.
10	6.38	0.07	0.05	0.03	0.02
20	6.26	0.14	0.10	0.07	0.03
30	6.14	0.21	0.14	0.10	0.04
40	6.03	0.28	0.19	0.13	0.06
50	5.91	0.35	0.23	0.16	0.07
60	5.80	0.41	0.28	0.19	0.09
70	5.69	0.48	0.32	0.22	0.10
80	5.59	0.55	0.36	0.25	0.12
90	5.48	0.61	0.41	0.28	0.13
100	5.38	0.67	0.45	0.30	0.14
110	5.28	0.73	0.49	0.33	0.16
120	5.18	0.79	0.53	0.36	0.17
130	5.09	0.85	0.57	0.38	0.18
140	4.99	0.91	0.60	0.41	0.20
150	4.90	0.96	0.64	0.43	0.21
160	4.81	1.02	0.68	0.46	0.22
170	4.72	1.07	0.72	0.48	0.23
180	4.63	1.12	0.75	0.50	0.25
190	4.54	1.17	0.78	0.52	0.26
200	4.46	1.23	0.82	0.55	0.27
210	4.37	1.28	0.85	0.57	0.28
220	4.29	1.33	0.88	0.59	0.29
230	4.21	1.37	0.92	0.61	0.31
240	4.13	1.42	0.95	0.63	0.32
250	4.05	1.47	0.98	0.65	0.33
260	3.98	1.51	1.01	0.67	0.34
270	3.91	1.56	1.04	0.69	0.35
280	3.83	1.60	1.07	0.71	0.36
290	3.76	1.64	1.10	0.73	0.37
300	3.69	1.69	1.13	0.74	0.38

Test 19, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	3.62	1.73	1.15	0.76	0.39
320	3.55	1.76	1.17	0.78	0.40
330	3.49	1.81	1.21	0.79	0.41
340	3.42	1.85	1.23	0.81	0.42
350	3.36	1.89	1.26	0.83	0.43
360	3.29	1.92	1.28	0.84	0.44
370	3.23	1.96	1.31	0.86	0.45
380	3.17	1.99	1.34	0.87	0.46
390	3.11	2.03	1.35	0.88	0.47
400	3.06	2.07	1.38	0.90	0.48
410	2.99	2.11	1.40	0.91	0.49
420	2.94	2.16	1.42	0.93	0.50
430	2.89	2.17	1.45	0.94	0.51
440	2.83	2.20	1.47	0.95	0.51
450	2.78	2.23	1.48	0.97	0.52
460	2.73	2.26	1.51	0.98	0.53
470	2.68	2.29	1.53	0.99	0.54
480	2.63	2.32	1.55	1.00	0.55
490	2.58	2.36	1.57	1.01	0.56
500	2.53	2.38	1.59	1.03	0.57

Test 20
Initial Conditions
Reactor Temperature: 22.3°C
Reactor Pressure: 407.3 mm
Acetaldehyde Pressure: 92.3 mm
Nitrogen Dioxide Pressure: 0.02192 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	11.91	0.	0.	0.	0.
10	11.61	0.18	0.12	0.08	0.04
20	11.31	0.36	0.24	0.16	0.08
30	11.01	0.53	0.35	0.24	0.11
40	10.74	0.69	0.47	0.32	0.15
50	10.47	0.86	0.58	0.39	0.18
60	10.19	1.02	0.68	0.46	0.21
70	9.95	1.18	0.79	0.53	0.25
80	9.68	1.33	0.90	0.59	0.29
90	9.44	1.48	0.99	0.68	0.31
100	9.20	1.63	1.08	0.72	0.35
110	8.96	1.77	1.18	0.79	0.38
120	8.73	1.90	1.26	0.85	0.41
130	8.50	2.04	1.36	0.90	0.45
140	8.29	2.18	1.44	0.97	0.48
150	8.08	2.30	1.52	1.02	0.51
160	7.88	2.43	1.60	1.07	0.53
170	7.67	2.53	1.69	1.13	0.56
180	7.47	2.66	1.76	1.19	0.59
190	7.30	2.77	1.85	1.23	0.61
200	7.10	2.88	1.92	1.27	0.65
210	6.92	2.99	1.99	1.31	0.67
220	6.74	3.10	2.06	1.36	0.69
230	6.57	3.19	2.13	1.41	0.73
240	6.41	3.30	2.20	1.45	0.75
250	6.24	3.40	2.26	1.49	0.77
260	6.08	3.49	2.32	1.54	0.80
270	5.94	3.60	2.39	1.57	0.82
280	5.78	3.69	2.45	1.60	0.85
290	5.64	3.77	2.51	1.63	0.86
300	5.48	3.85	2.58	1.67	0.89

Test 20, continued

Time (min)	NO_2	Concentration (10^{-7} moles/liter) NO	CO_2	CH_3ONO	CH_3NO_2
310	5.34	3.94	2.62	1.71	0.91
320	5.22	4.19	2.67	1.73	0.94
330	5.08	4.11	2.73	1.77	0.95
340	4.95	4.18	2.78	1.80	0.97
350	4.81	4.25	2.83	1.83	1.00
360	4.70	4.33	2.88	1.85	1.02
370	4.58	4.41	2.93	1.90	1.04
380	4.45	4.48	2.99	1.91	1.06
390	4.35	4.54	3.02	1.94	1.08
400	4.23	4.60	3.08	1.97	1.09
410	4.13	4.67	3.11	1.98	1.11
420	4.02	4.73	3.15	2.01	1.15
430	3.91	4.79	3.19	2.05	1.16
440	3.81	4.85	3.23	2.05	1.17
450	3.72	4.91	3.27	2.07	1.19
460	3.63	4.98	3.31	2.08	1.20
470	3.53	5.02	3.35	2.12	1.23
480	3.45	5.08	3.39	2.14	1.24
490	3.36	5.13	3.42	2.16	1.26
500	3.27	5.18	3.46	2.18	1.28

Test 21
Initial Conditions
Reactor Temperature: 22.2°C
Reactor Pressure: 764.2 mm
Acetaldehyde Pressure: 95.3 mm
Nitrogen Dioxide Pressure: 0.01692 mm
Nitric Oxide Pressure: 0.000697 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	9.19	0.38	0.	0.	0.
10	8.96	0.52	0.10	0.07	0.03
20	8.71	0.66	0.19	0.13	0.06
30	8.49	0.80	0.28	0.19	0.09
40	8.26	0.93	0.37	0.25	0.12
50	8.05	1.06	0.46	0.31	0.15
60	7.84	1.19	0.54	0.36	0.18
70	7.62	1.31	0.62	0.42	0.21
80	7.42	1.43	0.70	0.47	0.23
90	7.24	1.54	0.77	0.52	0.26
100	7.05	1.66	0.88	0.57	0.28
110	6.85	1.78	0.93	0.62	0.31
120	6.68	1.88	1.00	0.67	0.34
130	6.51	1.99	1.07	0.71	0.36
140	6.34	2.08	1.14	0.76	0.38
150	6.16	2.18	1.21	0.80	0.41
160	6.02	2.29	1.27	0.84	0.43
170	5.85	2.38	1.34	0.88	0.45
180	5.70	2.47	1.40	0.92	0.48
190	5.56	2.56	1.46	0.96	0.50
200	5.40	2.64	1.52	0.99	0.52
210	5.25	2.74	1.56	1.03	0.54
220	5.12	2.83	1.63	1.06	0.56
230	5.00	2.91	1.67	1.10	0.58
240	4.86	2.98	1.73	1.13	0.60
250	4.72	3.05	1.78	1.16	0.62
260	4.61	3.14	1.83	1.19	0.64
270	4.49	3.19	1.87	1.22	0.66
280	4.37	3.27	1.93	1.25	0.68
290	4.25	3.35	1.97	1.27	0.70
300	4.14	3.41	2.03	1.30	0.72

Test 21, continued

Time (min)	NO_2	Concentration (10^{-7} moles/liter) NO	CO_2	CH_3ONO	CH_3NO_2
310	4.03	3.46	2.06	1.33	0.74
320	3.94	3.54	2.10	1.35	0.75
330	3.83	3.60	2.15	1.37	0.77
340	3.73	3.66	2.19	1.40	0.79
350	3.63	3.72	2.22	1.42	0.81
360	3.53	3.77	2.26	1.44	0.82
370	3.43	3.84	2.31	1.46	0.84
380	3.35	3.88	2.34	1.48	0.85
390	3.26	3.94	2.36	1.50	0.87
400	3.18	3.99	2.41	1.52	0.88
410	3.09	4.04	2.44	1.54	0.90
420	3.01	4.09	2.46	1.56	0.91
430	2.93	4.13	2.50	1.57	0.93
440	2.86	4.19	2.53	1.59	0.94
450	2.77	4.22	2.56	1.61	0.96
460	2.72	4.27	2.59	1.62	0.97
470	2.64	4.32	2.62	1.64	0.98
480	2.58	4.34	2.65	1.65	1.00
490	2.49	4.38	2.68	1.66	1.01
500	2.44	4.43	2.70	1.68	1.02

Test 22
Initial Conditions
Reactor Temperature: 22.1°C
Reactor Pressure: 773.4 mm
Acetaldehyde Pressure: 101.3
Nitrogen Dioxide Pressure: 0.01439 mm
Nitric Oxide Pressure: 0.001196 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	7.82	0.65	0.	0.	0.
10	7.60	0.78	0.09	0.06	0.03
20	7.39	0.91	0.17	0.11	0.06
30	7.20	1.04	0.25	0.17	0.08
40	6.99	1.15	0.33	0.22	0.11
50	6.80	1.26	0.41	0.27	0.14
60	6.61	1.38	0.49	0.32	0.16
70	6.42	1.49	0.56	0.37	0.19
80	6.25	1.59	0.63	0.42	0.21
90	6.07	1.70	0.70	0.46	0.24
100	5.91	1.81	0.77	0.51	0.26
110	5.73	1.90	0.82	0.55	0.28
120	5.58	1.99	0.89	0.59	0.31
130	5.44	2.08	0.96	0.63	0.33
140	5.28	2.18	1.02	0.67	0.35
150	5.12	2.26	1.08	0.70	0.37
160	4.99	2.36	1.13	0.74	0.39
170	4.84	2.42	1.19	0.77	0.41
180	4.72	2.51	1.24	0.81	0.43
190	4.59	2.58	1.29	0.84	0.45
200	4.47	2.67	1.34	0.87	0.47
210	4.34	2.73	1.39	0.90	0.49
220	4.22	2.81	1.43	0.93	0.51
230	4.10	2.88	1.49	0.96	0.53
240	3.99	2.94	1.53	0.99	0.55
250	3.88	3.02	1.56	1.01	0.57
260	3.77	3.07	1.61	1.04	0.58
270	3.66	3.14	1.66	1.06	0.60
280	3.56	3.21	1.70	1.09	0.62
290	3.46	3.26	1.74	1.11	0.64
300	3.37	3.31	1.77	1.13	0.65

Test 22, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	3.27	3.38	1.83	1.15	0.67
320	3.18	3.42	1.85	1.17	0.68
330	3.10	3.48	1.90	1.19	0.90
340	3.02	3.54	1.92	1.21	0.71
350	2.93	3.59	1.96	1.23	0.73
360	2.85	3.63	1.99	1.25	0.74
370	2.77	3.67	2.01	1.27	0.76
380	2.68	3.73	2.04	1.28	0.77
390	2.62	3.77	2.07	1.30	0.78
400	2.54	3.82	2.11	1.31	0.80
410	2.47	3.86	2.15	1.33	0.81
420	2.41	3.90	2.17	1.34	0.83
430	2.34	3.95	2.19	1.36	0.84
440	2.27	3.98	2.22	1.37	0.85
450	2.22	4.02	2.24	1.38	0.86
460	2.16	4.05	2.27	1.39	0.87
470	2.09	4.09	2.29	1.41	0.89
480	2.02	4.12	2.32	1.42	0.90
490	1.98	4.16	2.35	1.43	0.91
500	1.92	4.19	2.36	1.44	0.92

Test 23
Initial Conditions
Reactor Temperature: 22.0°C
Reactor Pressure: 757.2 mm
Acetaldehyde Pressure: 87.7 mm
Nitrogen Dioxide Pressure: 0.01821 mm
Nitric Oxide Pressure: 0.002338 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	9.89	1.27	0.	0.	0.
10	9.65	1.41	0.09	0.06	0.03
20	9.42	1.55	0.19	0.12	0.06
30	9.20	1.69	0.28	0.18	0.09
40	8.99	1.82	0.36	0.24	0.12
50	8.76	1.95	0.45	0.30	0.05
60	8.56	2.06	0.53	0.35	0.18
70	8.34	2.19	0.62	0.41	0.21
80	8.14	2.31	0.70	0.46	0.24
90	7.96	2.44	0.77	0.51	0.26
100	7.77	2.54	0.85	0.56	0.29
110	7.58	2.65	0.92	0.60	0.32
120	7.39	2.76	1.00	0.65	0.34
130	7.22	2.88	1.07	0.70	0.37
140	7.05	2.97	1.14	0.74	0.40
150	6.88	3.07	1.20	0.78	0.42
160	6.73	3.17	1.28	0.82	0.44
170	6.56	3.27	1.33	0.86	0.47
180	6.40	3.36	1.40	0.90	0.49
190	6.26	3.45	1.46	0.94	0.52
200	6.09	3.54	1.52	0.98	0.54
210	5.95	3.62	1.57	1.01	0.56
220	5.81	3.72	1.62	1.05	0.58
230	5.67	3.81	1.69	1.08	0.60
240	5.54	3.88	1.74	1.11	0.63
250	5.41	3.95	1.79	1.15	0.65
260	5.28	4.04	1.85	1.18	0.67
270	5.14	4.11	1.90	1.21	0.69
280	5.04	4.19	1.94	1.24	0.71
290	4.91	4.26	1.99	1.26	0.73
300	4.79	4.33	2.04	1.29	0.75

Test 23, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	4.68	4.40	2.09	1.32	0.77
320	4.57	4.46	2.14	1.34	0.79
330	4.46	4.52	2.17	1.37	0.81
340	4.35	4.59	2.22	1.39	0.82
350	4.25	4.66	2.26	1.42	0.84
360	4.14	4.72	2.30	1.44	0.86
370	4.05	4.78	2.34	1.46	0.88
380	3.96	4.83	2.38	1.48	0.89
390	3.86	4.88	2.41	1.50	0.91
400	3.76	4.95	2.44	1.52	0.93
410	3.67	5.01	2.49	1.54	0.94
420	3.59	5.05	2.51	1.56	0.96
430	3.49	5.10	2.56	1.58	0.98
440	3.42	5.15	2.60	1.60	0.99
450	3.33	5.20	2.62	1.61	1.01
460	3.26	5.24	2.65	1.63	1.02
470	3.18	5.30	2.69	1.65	1.04
480	3.09	5.34	2.72	1.66	1.05
490	3.03	5.39	2.74	1.68	1.07
500	2.96	5.43	2.77	1.69	1.08

Test 24
Initial Conditions
Reactor Temperature: 22.5°C
Reactor Pressure: 768.7 mm
Acetaldehyde Pressure: 114.2 mm
Nitrogen Dioxide Pressure: 0.01540 mm
Nitric Oxide Pressure: 0.002490 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	8.37	1.35	0.	0.	0.
10	8.11	1.51	0.11	0.07	0.04
20	7.86	1.67	0.21	0.14	0.07
30	7.59	1.81	0.31	0.20	0.10
40	7.36	1.96	0.40	0.27	0.14
50	7.14	2.11	0.50	0.33	0.17
60	6.90	2.23	0.59	0.38	0.20
70	6.69	2.36	0.67	0.44	0.23
80	6.47	2.48	0.76	0.49	0.26
90	6.28	2.61	0.84	0.55	0.29
100	6.07	2.73	0.93	0.60	0.32
110	5.88	2.85	1.00	0.64	0.35
120	5.69	2.97	1.06	0.69	0.38
130	5.51	3.07	1.14	0.73	0.41
140	5.35	3.16	1.21	0.78	0.43
150	5.17	3.27	1.29	0.82	0.46
160	5.01	3.36	1.34	0.86	0.49
170	4.85	3.47	1.42	0.90	0.51
180	4.70	3.56	1.47	0.83	0.54
190	4.55	3.65	1.53	0.97	0.56
200	4.40	3.73	1.59	1.00	0.58
210	4.27	3.82	1.61	1.04	0.61
220	4.13	3.90	1.70	1.07	0.63
230	3.99	3.97	1.74	1.09	0.65
240	3.87	4.05	1.80	1.13	0.67
250	3.74	4.12	1.85	1.15	0.69
260	3.63	4.20	1.90	1.18	0.72
270	3.52	4.26	1.93	1.21	0.74
280	3.41	4.32	1.99	1.23	0.76
290	3.31	4.40	2.04	1.25	0.78
300	3.19	4.46	2.06	1.28	0.79

Test 24, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	3.09	4.53	2.10	1.30	0.81
320	3.00	4.58	2.16	1.32	0.83
330	2.89	4.63	2.19	1.34	0.85
340	2.82	4.70	2.22	1.36	0.87
350	2.72	4.74	2.26	1.37	0.88
360	2.64	4.79	2.29	1.39	0.90
370	2.54	4.84	2.33	1.41	0.92
380	2.46	4.89	2.37	1.43	0.93
390	2.39	4.95	2.38	1.44	0.95
400	2.32	4.99	2.41	1.46	0.97
410	2.24	5.04	2.44	1.47	0.98
420	2.17	5.06	2.49	1.48	1.00
430	2.10	5.11	2.51	1.50	1.01
440	2.05	5.15	2.53	1.51	1.03
450	1.97	5.19	2.56	1.52	1.04
460	1.90	5.24	2.58	1.53	1.05
470	1.85	5.26	2.61	1.54	1.07
480	1.79	5.30	2.63	1.55	1.08
490	1.74	5.33	2.65	1.56	1.09
500	1.68	5.37	2.68	1.57	1.11

Test 25
Initial Conditions
Reactor Temperature: 21.9°C
Reactor Pressure: 758.6 mm
Acetaldehyde Pressure: 78.6 mm
Nitrogen Dioxide Pressure: 0.01787 mm
Nitric Oxide Pressure: 0.003683 mm

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	9.71	2.00	0.	0.	0.
10	9.50	2.12	0.08	0.05	0.03
20	9.30	2.25	0.16	0.11	0.06
30	9.10	2.36	0.24	0.16	0.08
40	8.91	2.47	0.32	0.21	0.11
50	8.72	2.59	0.40	0.26	0.14
60	8.54	2.70	0.47	0.31	0.16
70	8.36	2.81	0.54	0.35	0.19
80	8.19	2.93	0.61	0.40	0.21
90	8.01	3.02	0.68	0.44	0.24
100	7.84	3.13	0.75	0.49	0.26
110	7.68	3.23	0.82	0.53	0.29
120	7.51	3.32	0.88	0.57	0.31
130	7.35	3.42	0.95	0.61	0.34
140	7.18	3.51	1.01	0.65	0.36
150	7.05	3.60	1.07	0.69	0.38
160	6.90	3.69	1.14	0.72	0.41
170	6.74	3.77	1.19	0.76	0.43
180	6.61	3.87	1.24	0.79	0.45
190	6.47	3.95	1.30	0.83	0.47
200	6.32	4.03	1.35	0.86	0.49
210	6.20	4.11	1.41	0.89	0.51
220	6.06	4.19	1.45	0.93	0.53
230	5.94	4.26	1.51	0.96	0.56
240	5.80	4.35	1.56	0.99	0.58
250	5.69	4.43	1.61	1.02	0.60
260	5.56	4.49	1.66	1.05	0.62
270	5.43	4.56	1.69	1.07	0.63
280	5.33	4.62	1.75	1.10	0.65
290	5.21	4.71	1.81	1.13	0.67
300	5.10	4.77	1.84	1.15	0.69

Test 25, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	4.99	4.83	1.89	1.18	0.71
320	4.89	4.89	1.94	1.20	0.73
330	4.78	4.96	1.96	1.23	0.75
340	4.68	5.02	2.00	1.25	0.76
350	4.58	5.08	2.05	1.27	0.78
360	4.49	5.14	2.10	1.29	0.80
370	4.39	5.19	2.13	1.31	0.81
380	4.30	5.26	2.17	1.33	0.83
390	4.21	5.30	2.19	1.35	0.85
400	4.12	5.36	2.24	1.37	0.86
410	4.04	5.42	2.27	1.39	0.88
420	3.94	5.45	2.31	1.41	0.89
430	3.86	5.51	2.34	1.43	0.91
440	3.79	5.55	2.37	1.45	0.93
450	3.71	5.62	2.40	1.46	0.94
460	3.62	5.66	2.44	1.48	0.96
470	3.54	5.70	2.47	1.50	0.97
480	3.47	5.75	2.50	1.51	0.99
490	3.39	5.78	2.53	1.53	1.00
500	3.32	5.83	2.56	1.54	1.01

Test 26
Initial Conditions
Reactor Temperature: 22.0°C
Reactor Pressure: 761.2 mm
Acetaldehyde Pressure: 85.4 mm
Nitrogen Dioxide Pressure: 0.01325 mm
Glass Beads in Reactor

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	7.20	0.	0.	0.	0.
10	7.03	0.10	0.07	0.05	0.02
20	6.86	0.20	0.13	0.09	0.04
30	6.70	0.30	0.20	0.14	0.06
40	6.54	0.39	0.26	0.18	0.08
50	6.39	0.49	0.32	0.22	0.10
60	6.24	0.58	0.38	0.26	0.12
70	6.10	0.67	0.44	0.30	0.14
80	5.94	0.75	0.50	0.34	0.16
90	5.80	0.84	0.56	0.38	0.18
100	5.67	0.92	0.61	0.41	0.20
110	5.53	1.01	0.66	0.45	0.22
120	5.40	1.08	0.72	0.48	0.24
130	5.27	1.15	0.76	0.52	0.25
140	5.14	1.24	0.83	0.56	0.28
150	5.03	1.30	0.87	0.58	0.29
160	4.92	1.37	0.92	0.61	0.30
170	4.79	1.44	0.96	0.64	0.32
180	4.68	1.51	1.01	0.67	0.34
190	4.57	1.58	1.05	0.70	0.35
200	4.45	1.64	1.09	0.73	0.37
210	4.35	1.70	1.14	0.75	0.38
220	4.25	1.77	1.18	0.78	0.40
230	4.15	1.83	1.23	0.81	0.41
240	4.05	1.89	1.26	0.83	0.43
250	3.96	1.94	1.30	0.86	0.44
260	3.86	1.99	1.33	0.88	0.46
270	3.77	2.05	1.36	0.90	0.47
280	3.68	2.12	1.41	0.92	0.48
290	3.60	2.15	1.44	0.94	0.50
300	3.50	2.21	1.47	0.97	0.51

Test 26, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	3.43	2.26	1.51	0.99	0.52
320	3.34	2.31	1.53	1.01	0.54
330	3.27	2.36	1.57	1.02	0.55
340	3.18	2.40	1.60	1.04	0.56
350	3.11	2.44	1.63	1.05	0.57
360	3.04	2.49	1.66	1.08	0.58
370	2.96	2.54	1.69	1.10	0.60
380	2.90	2.58	1.72	1.11	0.61
390	2.82	2.61	1.75	1.13	0.62
400	2.76	2.66	1.77	1.14	0.63
410	2.70	2.70	1.80	1.16	0.64
420	2.63	2.74	1.83	1.17	0.65
430	2.57	2.77	1.84	1.19	0.66
440	2.51	2.81	1.88	1.20	0.67
450	2.45	2.85	1.90	1.21	0.69
460	2.39	2.88	1.92	1.23	0.70
470	2.34	2.92	1.94	1.24	0.71
480	2.28	2.94	1.97	1.25	0.72
490	2.23	2.98	1.99	1.26	0.73
500	2.17	3.01	2.02	1.27	0.74

Test 27
Initial Conditions
Reactor Temperature: 22.0°C
Reactor Pressure: 752.8 mm
Acetaldehyde Pressure: 40.9 mm
Nitrogen Dioxide Pressure: 0.01217 mm
Glass Beads in Reactor

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	6.61	0.	0.	0.	0.
10	6.53	0.05	0.03	0.02	0.01
20	6.46	0.09	0.06	0.04	0.02
30	6.39	0.13	0.09	0.06	0.03
40	6.31	0.18	0.12	0.08	0.04
50	6.24	0.22	0.15	0.10	0.05
60	6.17	0.26	0.18	0.12	0.06
70	6.10	0.31	0.20	0.14	0.06
80	6.03	0.35	0.24	0.16	0.07
90	5.96	0.39	0.26	0.18	0.08
100	5.89	0.43	0.29	0.19	0.09
110	5.83	0.47	0.31	0.21	0.10
120	5.76	0.51	0.34	0.23	0.11
130	5.69	0.56	0.37	0.25	0.12
140	5.62	0.59	0.39	0.27	0.13
150	5.57	0.63	0.42	0.28	0.13
160	5.50	0.66	0.44	0.30	0.14
170	5.43	0.70	0.47	0.32	0.15
180	5.38	0.74	0.49	0.33	0.16
190	5.32	0.78	0.52	0.35	0.17
200	5.26	0.81	0.54	0.37	0.18
210	5.20	0.85	0.57	0.38	0.18
220	5.14	0.88	0.59	0.40	0.19
230	5.09	0.92	0.61	0.41	0.20
240	5.02	0.95	0.64	0.43	0.21
250	4.96	0.99	0.66	0.44	0.22
260	4.92	1.02	0.68	0.46	0.22
270	4.85	1.05	0.70	0.47	0.23
280	4.80	1.09	0.73	0.49	0.24
290	4.74	1.12	0.75	0.50	0.25
300	4.69	1.15	0.77	0.52	0.25

Test 27, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	4.63	1.19	0.79	0.53	0.26
320	4.58	1.21	0.81	0.54	0.27
330	4.52	1.25	0.83	0.56	0.28
340	4.48	1.28	0.85	0.57	0.28
350	4.43	1.29	0.87	0.58	0.29
360	4.38	1.35	0.89	0.60	0.30
370	4.33	1.38	0.91	0.61	0.30
380	4.28	1.41	0.93	0.62	0.31
390	4.24	1.43	0.95	0.63	0.32
400	4.17	1.46	0.97	0.65	0.32
410	4.13	1.48	0.99	0.66	0.33
420	4.08	1.51	1.01	0.67	0.34
430	4.03	1.54	1.01	0.68	0.35
440	3.99	1.58	1.05	0.69	0.35
450	3.95	1.61	1.06	0.71	0.36
460	3.90	1.62	1.08	0.72	0.36
470	3.87	1.65	1.10	0.73	0.37
480	3.81	1.67	1.12	0.74	0.38
490	3.77	1.70	1.14	0.75	0.38
500	3.74	1.73	1.15	0.76	0.39

Test 28
Initial Conditions
Reactor Temperature: 21.8°C
Reactor Pressure: 759.1 mm
Acetaldehyde Pressure: 102.7 mm
Nitrogen Dioxide Pressure: 9.02106 mm
Glass Beads in Reactor

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	11.44	0.	0.	0.	0.
10	11.11	0.20	0.13	0.09	0.04
20	10.80	0.38	0.26	0.18	0.08
30	10.48	0.58	0.39	0.26	0.12
40	10.18	0.76	0.51	0.34	0.16
50	9.87	0.94	0.62	0.42	0.20
60	9.60	1.11	0.74	0.50	0.24
70	9.33	1.27	0.86	0.57	0.27
80	9.05	1.43	0.96	0.65	0.31
90	8.79	1.58	1.05	0.71	0.35
100	8.53	1.74	1.16	0.78	0.38
110	8.30	1.88	1.25	0.85	0.41
120	8.05	2.03	1.36	0.91	0.45
130	7.82	2.17	1.46	0.97	0.48
140	7.58	2.32	1.55	1.03	0.51
150	7.37	2.44	1.62	1.08	0.54
160	7.17	2.58	1.71	1.14	0.57
170	6.95	2.69	1.80	1.19	0.60
180	6.74	2.81	1.88	1.24	0.63
190	6.56	2.92	1.95	1.29	0.66
200	6.37	3.04	2.04	1.34	0.69
210	6.18	3.15	2.10	1.39	0.72
220	6.00	3.26	2.17	1.43	0.74
230	5.82	3.37	2.24	1.47	0.77
240	5.66	3.47	2.30	1.51	0.80
250	5.50	3.56	2.38	1.55	0.82
260	5.33	3.67	2.45	1.59	0.85
270	5.19	3.74	2.49	1.63	0.87
280	5.04	3.83	2.55	1.66	0.90
290	4.89	3.94	2.62	1.70	0.92
300	4.74	4.01	2.68	1.73	0.94

Test 28, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	4.61	4.10	2.72	1.76	0.97
320	4.49	4.18	2.78	1.80	0.99
330	4.35	4.25	2.84	1.83	1.01
340	4.22	4.33	2.89	1.85	1.03
350	4.10	4.40	2.93	1.88	1.05
360	3.98	4.47	2.98	1.91	1.07
370	3.88	4.54	3.03	1.93	1.09
380	3.76	4.62	3.07	1.96	1.11
390	3.66	4.67	3.12	1.98	1.13
400	3.54	4.74	3.17	2.01	1.15
410	3.43	4.81	3.21	2.03	1.17
420	3.34	4.86	3.23	2.05	1.19
430	3.25	4.92	3.28	2.07	1.21
440	3.14	4.97	3.32	2.09	1.23
450	3.06	5.03	3.34	2.11	1.24
460	2.97	5.08	3.39	2.13	1.26
470	2.89	5.12	3.41	2.14	1.28
480	2.80	5.18	3.45	2.16	1.29
490	2.72	5.22	3.49	2.18	1.31
500	2.64	5.28	3.52	2.19	1.33

Test 29
Initial Conditions
Reactor Temperature: 22.4°C
Reactor Pressure: 774.3 mm
Acetaldehyde Pressure: 71.1 mm
Nitrogen Dioxide Pressure: 0.01992 mm
Glass Wool in Reactor

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	10.82	0.	0.	0.	0.
10	10.61	0.13	0.08	0.06	0.03
20	10.40	0.25	0.17	0.11	0.05
30	10.20	0.37	0.25	0.17	0.08
40	10.00	0.49	0.33	0.22	0.10
50	9.82	0.61	0.40	0.28	0.13
60	9.62	0.72	0.49	0.33	0.16
70	9.43	0.83	0.56	0.38	0.18
80	9.25	0.94	0.63	0.43	0.20
90	9.07	1.05	0.70	0.47	0.23
100	8.88	1.16	0.77	0.52	0.25
110	8.73	1.25	0.84	0.57	0.27
120	8.55	1.36	0.91	0.61	0.30
130	8.38	1.46	0.97	0.66	0.32
140	8.21	1.57	1.03	0.70	0.34
150	8.06	1.66	1.10	0.74	0.36
160	7.90	1.76	1.17	0.78	0.38
170	7.74	1.83	1.24	0.82	0.40
180	7.60	1.93	1.29	0.86	0.43
190	7.44	2.02	1.35	0.90	0.45
200	7.31	2.11	1.41	0.94	0.47
210	7.16	2.19	1.46	0.98	0.49
220	7.03	2.28	1.53	1.01	0.51
230	6.90	2.37	1.57	1.05	0.53
240	6.76	2.45	1.63	1.08	0.54
250	6.62	2.52	1.69	1.11	0.56
260	6.50	2.60	1.73	1.15	0.58
270	6.38	2.66	1.77	1.18	0.60
280	6.24	2.75	1.82	1.21	0.62
290	6.12	2.82	1.89	1.24	0.64
300	6.00	2.89	1.93	1.27	0.65

Test 29, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	5.89	2.97	1.97	1.30	0.67
320	5.77	3.04	2.03	1.33	0.70
330	5.66	3.10	2.06	1.36	0.71
340	5.54	3.15	2.11	1.38	0.72
350	5.44	3.23	2.14	1.41	0.74
360	5.34	3.30	2.19	1.44	0.76
370	5.23	3.34	2.23	1.46	0.77
380	5.13	3.41	2.28	1.49	0.79
390	5.03	3.47	2.32	1.51	0.80
400	4.93	3.52	2.35	1.53	0.82
410	4.85	3.60	2.39	1.56	0.84
420	4.74	3.65	2.43	1.58	0.85
430	4.65	3.69	2.47	1.62	0.87
440	4.56	3.76	2.50	1.62	0.88
450	4.47	3.82	2.55	1.64	0.90
460	4.39	3.85	2.57	1.66	0.91
470	4.29	3.90	2.61	1.68	0.92
480	4.22	3.95	2.63	1.70	0.94
490	4.14	4.01	2.67	1.72	0.95
500	4.05	4.06	2.71	1.74	0.97

Test 30
Initial Conditions
Reactor Temperature: 23.3°C
Reactor Pressure: 766.8 mm
Acetaldehyde Pressure: 118.6 mm
Nitrogen Dioxide Pressure: 0.02583 mm
Glass Wool in Reactor

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
0	14.03	0.	0.	0.	0.
10	13.57	0.28	0.18	0.13	0.06
20	13.13	0.54	0.36	0.25	0.11
30	12.71	0.80	0.53	0.36	0.17
40	12.28	1.05	0.70	0.47	0.22
50	11.83	1.29	0.86	0.58	0.28
60	11.49	1.52	1.01	0.66	0.33
70	11.12	1.75	1.16	0.79	0.38
80	10.75	1.96	1.31	0.88	0.43
90	10.40	2.18	1.45	0.97	0.48
100	10.06	2.38	1.59	1.06	0.52
110	9.74	2.58	1.72	1.15	0.57
120	9.42	2.77	1.84	1.23	0.61
130	9.10	2.94	1.97	1.31	0.66
140	8.81	3.13	2.09	1.39	0.70
150	8.52	3.30	2.20	1.46	0.74
160	8.24	3.47	2.31	1.53	0.78
170	7.98	3.63	2.42	1.60	0.82
180	7.71	3.79	2.53	1.67	0.86
190	7.46	3.94	2.63	1.73	0.90
200	7.21	4.09	2.72	1.79	0.94
210	6.98	4.23	2.82	1.85	0.97
220	6.75	4.36	2.91	1.90	1.01
230	6.54	4.50	3.00	1.96	1.04
240	6.32	4.62	3.08	2.01	1.08
250	6.12	4.75	3.17	2.06	1.11
260	5.91	4.87	3.25	2.10	1.14
270	5.72	4.98	3.32	2.15	1.17
280	5.53	5.10	3.40	2.19	1.20
290	5.35	5.20	3.47	2.23	1.24
300	5.19	5.31	3.54	2.27	1.27

Test 30, continued

Time (min)	Concentration (10^{-7} moles/liter) NO_2	NO	CO_2	CH_3ONO	CH_3NO_2
310	5.00	5.40	3.61	2.31	1.29
320	4.84	5.52	3.67	2.35	1.32
330	4.69	5.60	3.74	2.38	1.34
340	4.53	5.69	3.80	2.43	1.39
350	4.39	5.78	3.86	2.44	1.41
360	4.24	5.86	3.91	2.48	1.43
370	4.10	5.95	3.98	2.51	1.46
380	3.96	6.03	4.02	2.54	1.48
390	3.84	6.11	4.08	2.57	1.51
400	3.72	6.19	4.13	2.59	1.53
410	3.59	6.26	4.17	2.62	1.56
420	3.48	6.33	4.22	2.64	1.59
430	3.36	6.40	4.27	2.67	1.60
440	3.25	6.47	4.31	2.69	1.62
450	3.15	6.53	4.35	2.71	1.65
460	3.04	6.58	4.39	2.73	1.66
470	2.94	6.64	4.43	2.75	1.69
480	2.85	6.69	4.47	2.76	1.71
490	2.75	6.76	4.51	2.78	1.73
500	2.67	6.82	4.55	2.80	1.75

APPENDIX B

Electron-Capture Detector

The theory of the electron-capture detector and the optimum conditions for the quantitative analysis of ppm concentrations of nitrogen dioxide are discussed.

APPENDIX B

Electron-Capture Detector

Introduction

In this experiment, the electron-capture detector was used for the quantitative analysis of ppm concentrations of nitrogen dioxide, carbon dioxide, methyl nitrite and nitromethane. Since 1957, ionization detectors have been developed which have very high sensitivity to specific compounds. The electron-capture detector[B.1-B.7] is very sensitive to compounds with high affinities for free electrons. The electron-capture detector has been used for the quantitative determination of picagram quantities of compounds with halogen, sulfur, phosphorous, oxygen and nitrogen substituents.

Theory

The electron-capture detector is based on the fact that certain compounds have a high affinity for free electrons. The detector is a cylindrical vessel with a diameter and length of one centimeter. The chamber contains a beta-ray source, tritium or nickel 63, which creates a background current of about 10^{-9} amperes. A stream of inert carrier gas, which does not absorb electrons, flows through the detector. Nitrogen, argon and helium can be employed as carrier gases. The detector is connected to

to a potential source, dc or pulse, and the electrodes connected to an instrument for measuring the resulting current.

When the electron-capturing compound enters the detector, it reacts with an electron to form a negative ion

$$e^- + AB \longrightarrow AB^- \pm \text{Energy} \qquad \text{(B.1)}$$

or a neutral radical and a negative ion

$$e^- + AB \longrightarrow A + B^- \pm \text{Energy} \qquad \text{(B.2)}$$

The net result is the removal of an electron from the system and the formation of a less mobile negative ion. When the pulsed potential is applied, essentially all the electrons within the cell are collected. However, at least one electron is lost for each molecule of electron-capturing compound. This loss of electrons causes a corresponding decrease in current between the electrodes. The decrease in current is proportional to the quantity of sample, is amplified and appears as a peak on a recorder for the gas chromatograph.

The parameters affecting the response of the electron-capture detector are (1)cell geometry, (2)beta-ray source, (3)chamber temperature, (4)carrier gas, (5)scavenger gas,

and (6)applied potential.

Experimental

The object of the investigation was to determine the optimum conditions for the quantitative analysis of ppm concentrations of nitrogen dioxide.

The electron-capture detectors considered were the Loenco 130 and a plane-parallel detector designed by Morrison[B.8-B.10]. Tritium foil with an activity between 150 and 300 mc was investigated as the beta-ray source. The temperature of the detector oven was varied between 20 and 200°C. Argon, nitrogen, helium, and 5% methane in argon were investigated as carrier and scavenger gases.

Pulse and dc potentials were considered as applied voltages. The dc voltage was varied between 0.5 and 100 volts. Pulse operation was studied as a function of pulse amplitude (0.2 to 100 volts), period (10^{-2} to 10^{3} kc), and width (0.05 to 10^{4} microseconds).

The parameters were considered for (1)stability of the background current, (2)sensitivity to nitrogen dioxide, and (3)reproducibility of the response. The response of the electron-capture detector was defined as the fraction decrease in background current for a sample:

$$\text{Response} = \frac{\text{Peak Height x Attenuation}}{\text{Background Current Deflection x Attenuation}}$$

Results

The electron-capture detector designed by Morrison was superior to the Loenco 130 with respect to stability, sensitivity and reproducibility.

Tritium foil was investigated as the beta-ray source. Increased activity of the tritium foil increased the background current and response, but also increased the noise level in proportion to the response and background current. Therefore, the sensitivity of the electron-capture detector was not a strong function of the strength of the beta-ray source. Tritium foil with an activity of 200 mc was used in the detector.

The electron-capture detector was operated at a temperature of 190°C. At temperatures near 200°C, greater background current stability, higher sensitivity to nitrogen dioxide, and increased linearity of the response were obtained. At lower temperatures, a higher absolute response was obtained, but baseline drift of the background current was a major problem.

The pulse mode of operation was superior to dc operation for an argon carrier and a 5% methane in argon carrier. Nitrogen carrier was excellent for dc operation, but was unsatisfactory for the pulse mode of operation. Helium carrier proved unsuccessful for both pulse and dc potentials. Since a very high flow rate of carrier gas

was required by the chromatography column, no scavenger gas was needed for the electron-capture detector.

The sensitivity of the electron-capture detector for pulse operation with an argon carrier was slightly superior to the dc potential with a nitrogen carrier. The pulse mode of operation provided better stability of the background current and a lower noise level.

Discussion

The background current of the electron-capture detector as a function of the flow rate of the argon carrier gas is presented in Figure B.1. The background current increased as the flow rate increased to 200 cc/min, but above 200 cc/min the background current was essentially independent of the flow rate of the carrier gas.

The background current of the electron-capture detector as a function of the pulse amplitude is illustrated in Figure B.2. The background current increased between 0.2 and 8 volts, maintained a maximum value between 8 and 22 volts, and slowly decreased between 22 and 100 volts.

The response to nitrogen dioxide as a function of the fraction on-time (pulse width/pulse period) is illustrated in Figure B.3. A maximum of the response was obtained for 0.01 on-time.

Conclusions

The optimum conditions were determined for the electron capture detector for the quantitative determination of nitrogen dioxide. In the concentration range between 1 and 10 ppm of nitrogen dioxide, the optimum parameters for the plane-parallel detector designed by Morrison were (1)a beta-ray source of tritium foil with an activity of 200 mc, (2)a detector temperature of 190°C, (3)an argon carrier gas with no scavenger gas, (4)a pulse amplitude of 8 volts, (5)a pulse period of 1000 microseconds, and (5)a pulse width of 10 microseconds.

A background current of 5.6×10^{-9} amperes was determined for the electron-capture detector at the optimum conditions. The limit of the response of the detector was 0.1 ppm of nitrogen dioxide.

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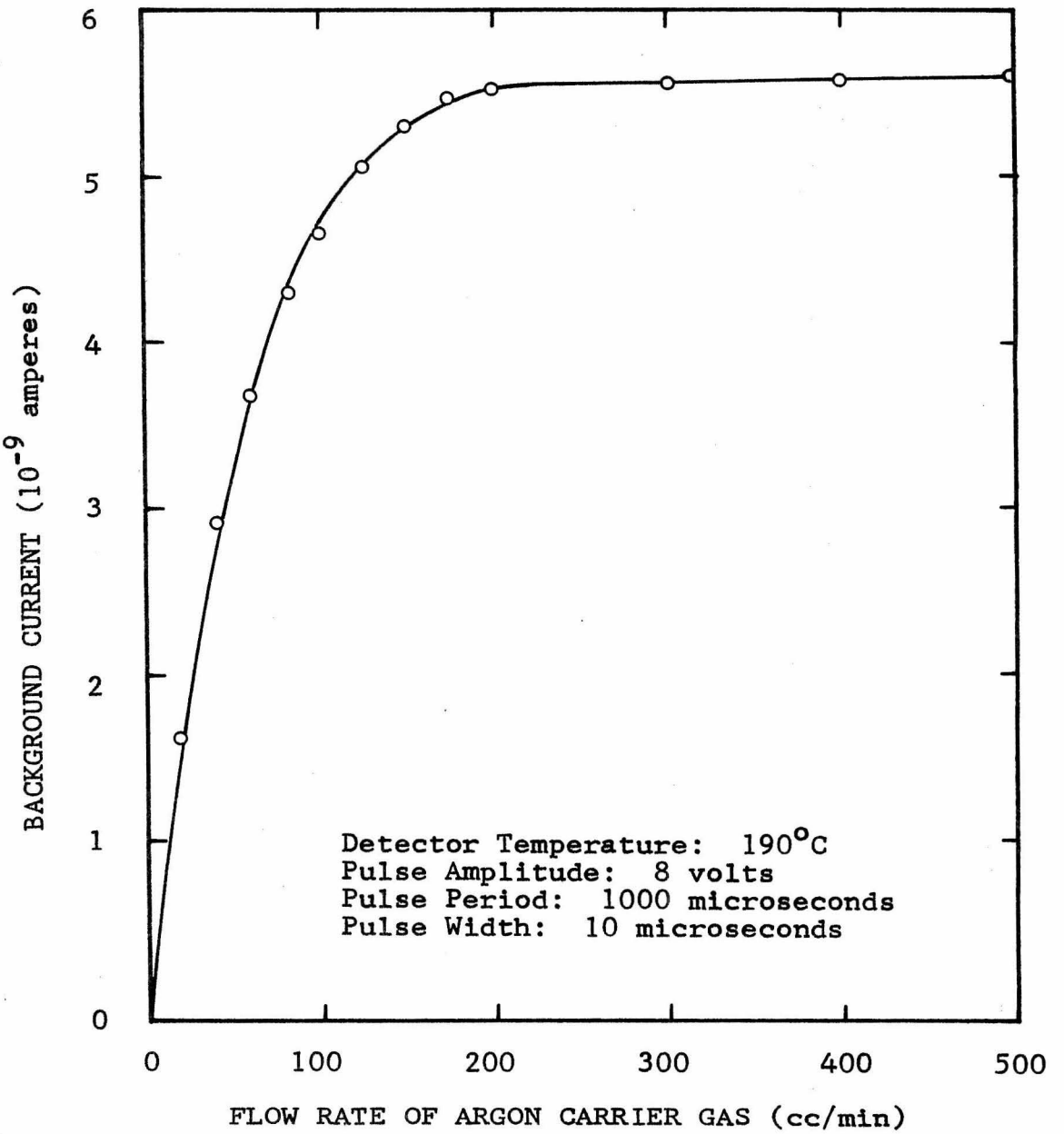

Figure B.1 The background current of the electron-capture detector as a function of the flow rate of argon carrier gas

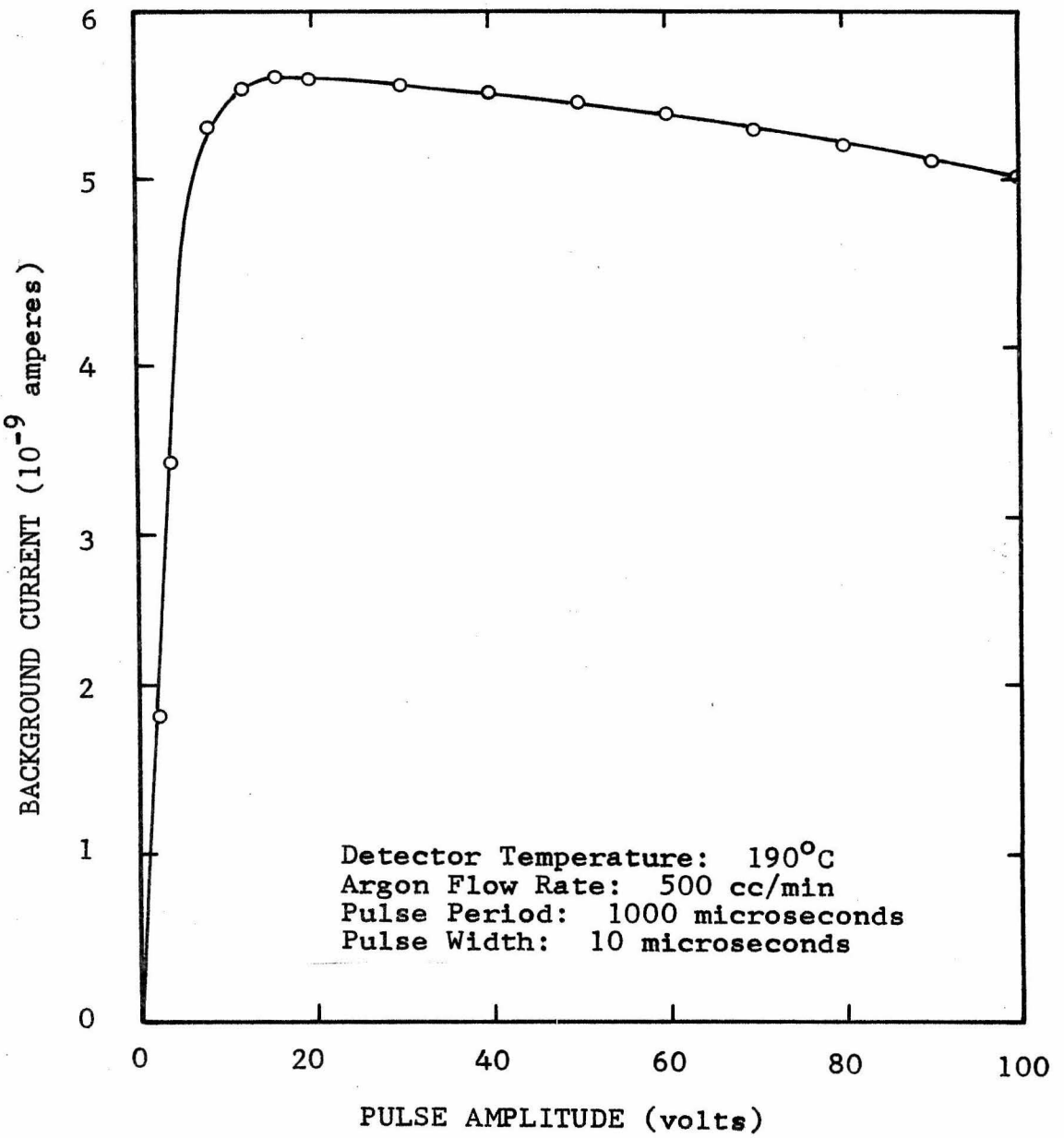

Figure B.2 The background current of the electron-capture detector as a function of the pulse amplitude.

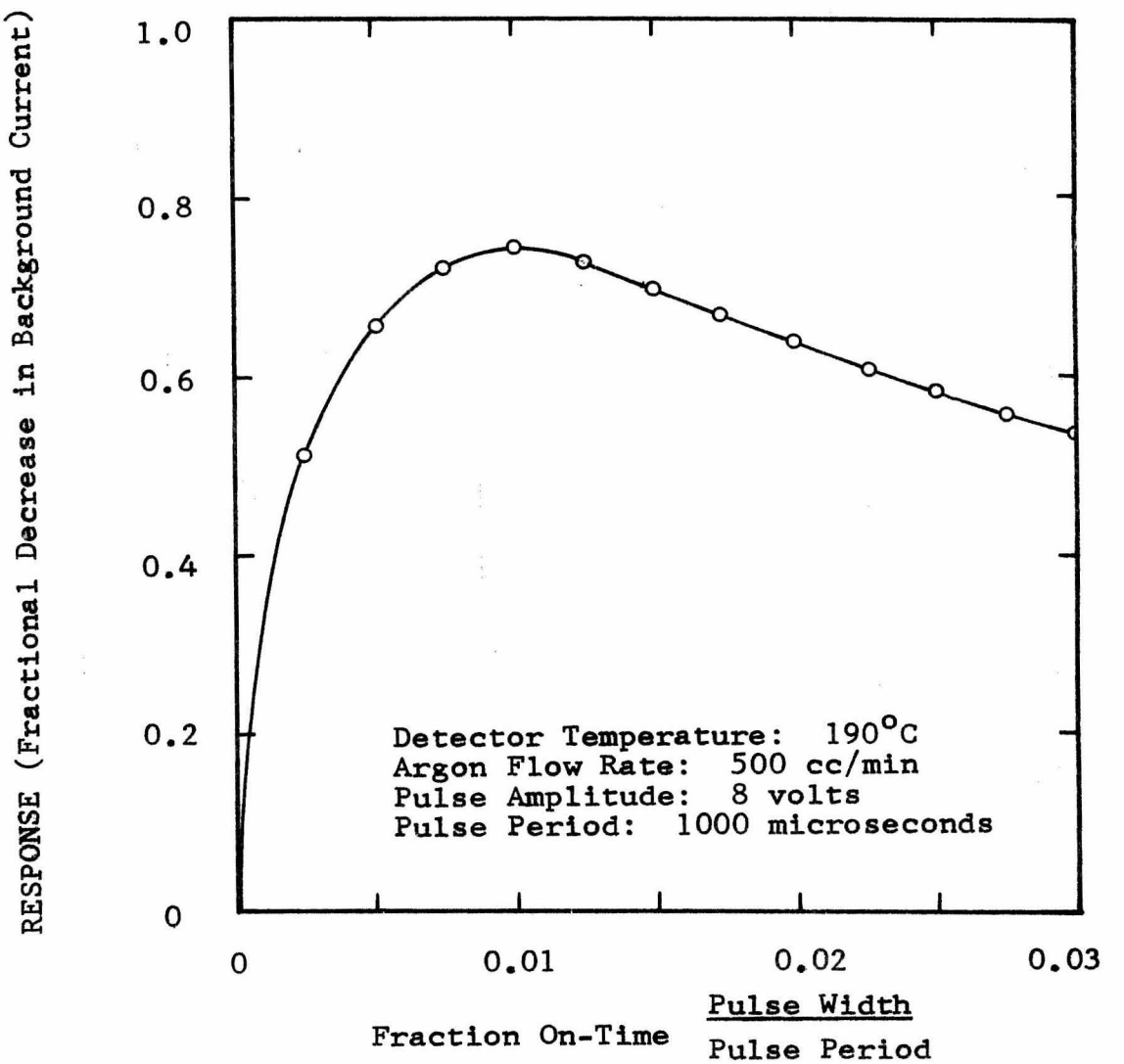

Figure B.3 The response of the electron-capture detector to nitrogen dioxide as a function of the fraction on-time of the pulse.

APPENDIX C

Gas Chromatography

The quantitative analysis by gas chromatography of the reactants and products of the reaction between acetaldehyde and nitrogen dioxide is discussed.

APPENDIX C

Gas Chromatography

Introduction

Gas-liquid chromatography[C.2,C.5] is a well-established technique for the analysis of organic and inorganic compounds. The reaction between acetaldehyde and nitrogen dioxide required the identification and quantitative determination of ppm concentrations of reactants and products in the presence of a large excess of acetaldehyde and diluent nitrogen. The experiment also required the analysis of trace amounts of possible secondary and tertiary products of the reaction.

Quantitative analysis by gas-liquid chromatography required a column for the separation of compounds and a detector for the selective determination of the components. The electron-capture detector was used for the analysis of inorganic gases and hydrocarbons with nitrogen and oxygen substituents. A column for the separation of nitrogen, nitric oxide, nitrogen dioxide, carbon dioxide, acetaldehyde, nitromethane, methyl nitrite, nitrous oxide and methyl nitrate[C.1,C.3,C.4,C.6,C.7] was needed in conjunction with the electron-capture detector. Acetaldehyde, methyl nitrite and nitromethane were monitored with a hydrogen flame-ionization detector, which was also used to

determine trace amounts of possible reaction products such as methane, ethane, acetone, biacetyl, acetic acid and methyl acetate. A column was also required for the separation of low molecular weight hydrocarbons[C.7,C.8,C.9] which might appear as products of the reaction between acetaldehyde and nitrogen dioxide.

Column Development

Columns were considered for the separation of the reactants and products of the reaction between acetaldehyde and nitrogen dioxide: nitrogen, nitrogen dioxide, nitric oxide, carbon dioxide, methyl nitrite, nitromethane and acetaldehyde. Possible secondary reaction products such as methyl nitrate, nitrous oxide and nitrated hydrocarbons, were also considered in the selection of columns. The primary problems were the separation and determination of ppm concentrations of nitrogen dioxide in the presence of a large excess of nitrogen, and the complete separation of nitrogen compounds.

Columns were also considered for the separation of low molecular weight hydrocarbons: paraffins, olefins, aldehydes, ketones, alcohols, acids and their elementary derivatives. Of principal interest was the separation of a large excess of acetaldehyde from trace quantities of methane, ethane, acetone, biacetyl, acetic acid and methyl

acetate.

The separation of a column was a function of (1)the polarity and weight fraction of the liquid phase, (2)the type and size of the solid support, (3)the diameter and length of the column, (4)the type of carrier gas and the flow rate, and (5)the temperature of the column.

Experimental

A systematic technique for the preparation of columns was developed. The solid support was rinsed and then dried overnight at 100°C. A weighed amount of the liquid phase (solute) was dissolved in a suitable solvent such as diethyl ether, acetone or benzene. A portion of the solid support was sieved and weighed, and then slowly mixed with the solution of solute and solvent. The resulting slurry was stirred for fifteen minutes and then the solvent was allowed to slowly evaporate in a hood or with a steam bath. Hi-purity dry nitrogen was passed over the slurry until the packing was "dry."

The columns were five or ten feet in length with an outside diameter of 1/8-inch. Stainless steel tubing with a wall thickness of 0.016 inch was used. The tubing was rinsed with diethyl ether, acetone and methanol, then dried with nitrogen. One end of the column was stoppered with a plug of siliconized glass wool. The packing was

poured into the column and tapped down. The packed column was coiled and placed in the chromatograph column oven where 50 cc/min of dry nitrogen was passed through it for twenty four hours. The column was conditioned by injection of 0.5 cc samples of nitrogen dioxide and hydrocarbons at five minute intervals until reproducible separation, retention times and peak heights were obtained.

The weight percent of the liquid phase on the solid support was varied between 0.5 and 20 percent. The length of the columns were either ten or twenty feet. Helium, argon and nitrogen were investigated as carrier gases. The flow rates of the carrier gases were varied between 10 and 500 cc/min. Scavenger gas was introduced for the lower flow rates. Column temperatures ranged from 20 to 250°C. The liquid phases and solid supports for the columns investigated are summarized in Table C.1.

Results

A column of 10% SF-96 on 40/80 mesh Fluoropak 80 with a length of twenty feet and an outside diameter of 1/8-inch, was used for the separation of inorganic gases and nitrated hydrocarbons. The identical separation was also obtained with a solid support of Teflon 6 with 10% SF-96. A sample chromatogram is illustrated in Figure C.1. The results for the electron-capture detector are summarized in Table C.2.

A column of Poropak Q with a length of twenty feet and an outside diameter of 1/8-inch, was used for the separation of the low molecular weight hydrocarbons. A sample chromatogram for the organic products of the reaction is illustrated in Figure C.2. The results for the hydrogen flame-ionization detector are presented in Table C.3

Discussion

SF-96, a non-polar methyl silicone oil, was the most successful liquid phase for the separation of nitrogen compounds. Fluoropak 80 and Teflon 6, inert solid supports, were superior to the active supports for the separation of the products of the reaction between acetaldehyde and nitrogen dioxide. The type and weight fraction of the liquid phase and solid support were the principal parameters affecting the separations. Small size column packing tended to pack tightly which caused a high pressure drop through the column and decreased the efficiency of the column. A low percentage of the liquid phase was difficult to prepare because the solute would not evenly coat the solid support.

The largest sample that the column could separate without overloading was 0.5 cc. The separation of the products of the reaction between acetaldehyde and nitrogen dioxide was increased by increasing the length of the column, but

this broadened the peaks and lengthened the tailing of the peaks. Increasing the temperature of the column from 20 to 250°C sharpened the peaks and lowered the retention times, but complete separation of the compounds was not accomplished. High flow rates of the carrier gas yielded distinct peaks and low retention times, however there was some overlapping of peaks. Therefore, a medium column length (20 ft), a low temperature for the column (22°C), and a high flow rate for the carrier gas (500 cc/min) was a compromise for fast analysis time, complete separation of the peaks and high responses for the compounds.

Conclusions

A column of 10 weight percent of SF-96 on 40/80 mesh Fluoropak 80, with a length of twenty feet and an outside diameter of 1/8-inch, was used for the separation of nitrogen, nitrogen dioxide, carbon dioxide, acetaldehyde, methyl nitrite and nitromethane. The optimum operating conditions for the column were (1)a flow rate of 500 cc/min for the argon carrier gas, (2)a column temperature of 22°C, and (3)a 0.5 cc sample size.

A column of 80/100 mesh Poropak Q, with a length of twenty feet and an outside diameter of 1/8-inch, was used for the separation of acetaldehyde and trace quantities of organic compounds. The optimum operating conditions were

(1)a flow rate of 50 cc/min for the helium carrier gas, (2)a column temperature of 180°C, and (3)a 0.5 cc sample size. The conditions for the hydrogen flame-ionization detector were (1)a detector temperature of 190°C, (2)a hydrogen flow rate of 60 cc/min, and (3)a flow rate of air of 350 cc/min.

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C.3 Morrison, M. E., Ph. D. Thesis, California Institute of Technology (1965).

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C.8 Wilhite, W. R., JPL Space Programs Summary, No. 37-40, vol. IV, Pasadena, California, 119 (1966).

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Table C.1 Liquid phases and solid supports for the columns investigated for the separation of inorganic gases and nitrated hydrocarbons.

Liquid Phase	Solid Support
Apiezon L	Chromosorb W (HMDS)
710 Silicone Oil	Chromosorb W (HMDS)
DC 200-500 Silicone Oil	Teflon 6
DC 703 Silicone Oil	Teflon 6
XF 1150 Silicone Oil	Teflon 6
SF-96 Silicone Oil	Teflon 6
SF-99 Silicone Oil	Teflon 6
SF-1017 Silicone Oil	Teflon 6
SF-96 Silicone Oil	Fluoropak 80
SF-99 Silicone Oil	Fluoropak 80
SF-96 Silicone Oil	Poropak P
none	Poropak P
SF-96 Silicone Oil	Poropak Q
none	Poropak Q
SF-96 Silicone Oil	Poropak R
none	Poropak R
SF-96 Silicone Oil	Poropak S
none	Poropak S
SF-96 Silicone Oil	Poropak T
none	Poropak T
SF-96 Silicone Oil	Poropak QS
none	Poropak QS
SF-96 Silicone Oil	Poropak N
none	Poropak N
none	Silica Gel

Table C.2 Operating conditions for the chromatography column and the electron-capture detector.

Column

Liquid Phase	SF-96
Weight Percent	10%
Solid Support	Fluoropak 80
Packing Size	40/80 mesh
Temperature	22°C
Carrier Gas	Argon
Flow Rate	500 cc/min
Column Length	20 ft
Sample Size	0.5 cc

Detector

Electron-Capture

Temperature	190°C
Scavenger Gas	None
Pulse Amplitude	8 volts
Pulse Period	1000 microseconds
Pulse Width	10 microseconds

Retention Times

Nitrogen	33 sec
Nitrogen Dioxide	38 sec
Carbon Dioxide	59 sec
Acetaldehyde	88 sec
Methyl Nitrite	169 sec
Nitromethane	327 sec

Table C.3 Operating conditions for the chromatography column and the hydrogen flame-ionization detector.

Column

Solid Phase	Poropak Q
Packing Size	40/80 mesh
Temperature	180°C
Carrier Gas	Helium
Flow Rate	50 cc/min
Column Length	20 ft
Sample Size	0.5 cc

Detector

Hydrogen Flame-Ionization

Temperature	190°C
Hydrogen Flow Rate	60 cc/min
Air Flow Rate	350 cc/min

Retention Times

Acetaldehyde	1.54 min
Methyl Nitrite	3.28 min
Nitromethane	6.27 min

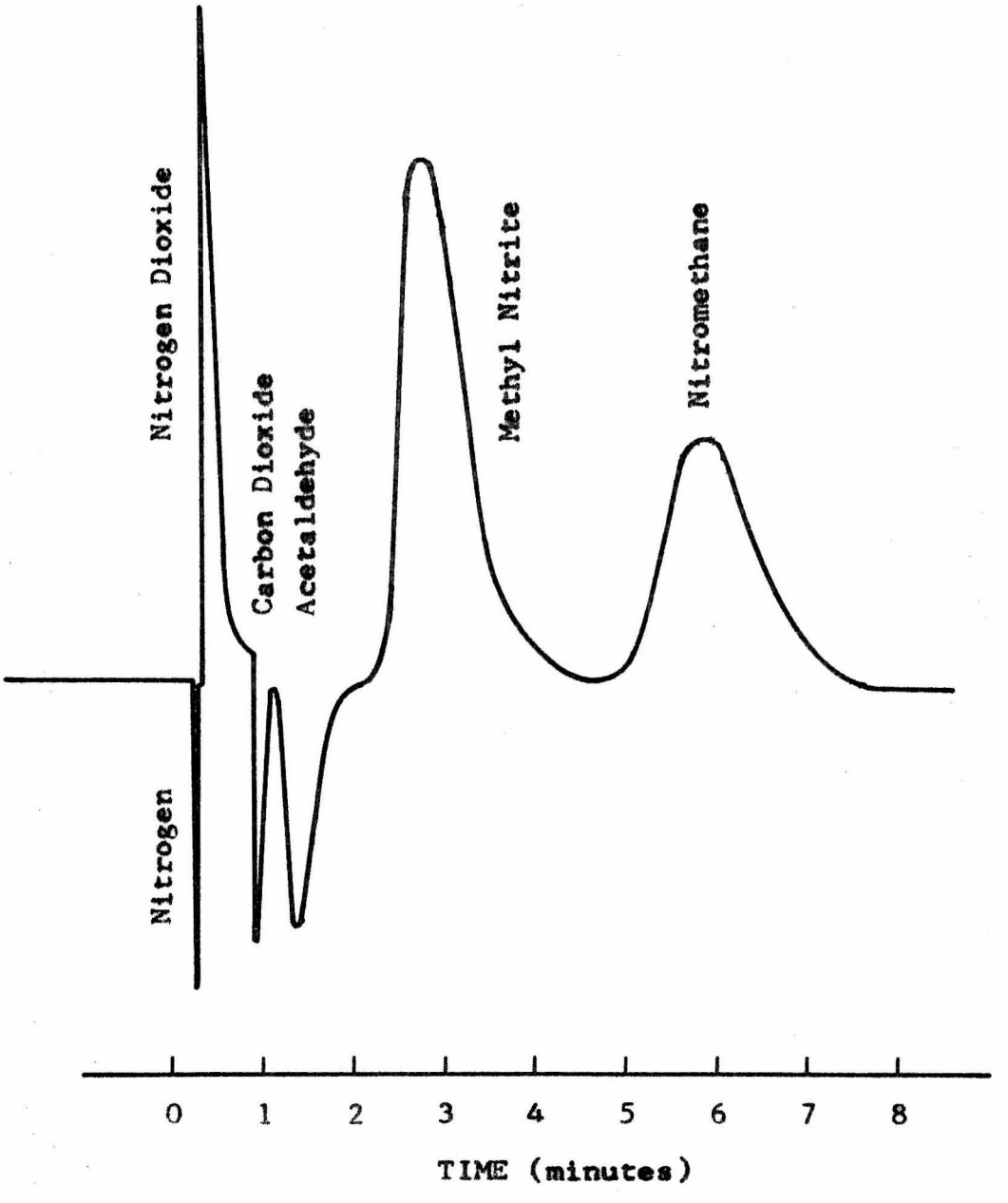


Figure C.1 Chromatogram for the SF-96 on Fluoropak 80 column with the electron-capture detector.

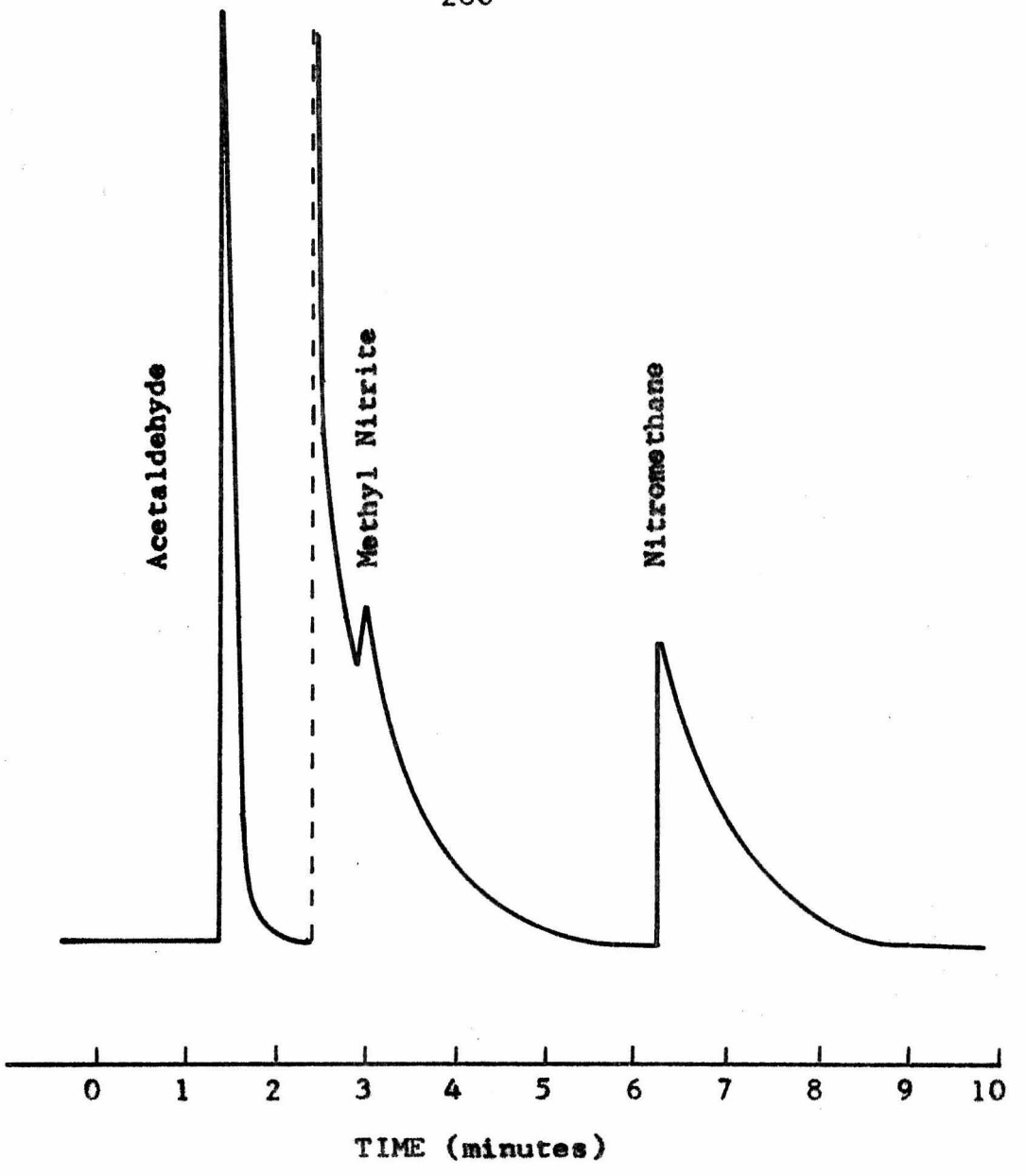


Figure C.2 Chromatogram for the Poropak Q column with the hydrogen flame-ionization detector.

APPENDIX D

Calibration

The calibration and sensitivity of the electron-capture detector and the hydrogen flame-ionization detector are presented for the reactants and products in the reaction between acetaldehyde and nitrogen dioxide.

APPENDIX D

Calibration

Introduction

The relationship between the concentration of a constituent and the response of a detector is the basis of quantitative analysis by gas chromatography. The change in background current in an ionization detector is proportional to the number of moles of a component in the sample. A decrease in background current is the response of the electron-capture detector. An increase in current is the response of the hydrogen flame-ionization detector. The changes in current appear as peaks on a chromatogram. The quantitative interpretation of a chromatogram depends upon relating the area under a peak or the height of a peak to the concentration of a constituent.

The absolute response method was the technique used for the quantitative determinations of reactants and products of the reaction between acetaldehyde and nitrogen dioxide. In the absolute response method, the response of the detector is compared to the concentration of the pure component. This method was superior to the internal standard method and the area normalization method because of the small number of components and the large differences in the shape of the peaks.

In order to obtain the concentrations of the reactants and products as functions of time, the response and sensitivity of the electron-capture detector and hydrogen flame-ionization detector were determined for each of the components. The response of the electron-capture detector (decrease in current/background current) as a function of the component concentration was determined for nitrogen dioxide, carbon dioxide, methyl nitrite and nitromethane. A detection limit was also determined for nitrous oxide and methyl nitrate, which were possible products of the reaction between acetaldehyde and nitrogen dioxide. The response of the hydrogen flame-ionization detector (area of the peak) as a function of concentration was obtained for acetaldehyde. In addition, a principal objective of the hydrogen flame-ionization detector was the quantitative identification of trace quantities of low molecular weight hydrocarbons which were possible products of the reaction between acetaldehyde and nitrogen dioxide. Therefore, the detection limits for nitromethane, methyl nitrite, methane, ethane, acetone, biacetyl, glyoxal, acetic acid and methyl acetate were also determined.

Experimental Method

The calibration curve for each compound was obtained by plotting the concentration of the pure compound versus

the response of the detector. The concentration of the compound was calculated assuming ideal gas behavior.

The response of the electron-capture detector was defined as the fraction decrease in background current:

$$\text{Response}_{ECD} = \frac{\text{Peak Height x Attenuation}}{\text{Background Current Deflection x Attenuation}}$$

The response of the flame-ionization detector was defined as the area of the peak:

$$\text{Response}_{FID} = \text{Peak Area x Attenuation}$$

A calibration curve for a compound defined the response of the detector as a function of the number of moles of the compound. The linear portion of the calibration curve determined the linearity of the detector for the compound. The detection limit of the detector for a component was defined as the minimum concentration that produced a response signal-to-noise ratio of two:

$$\frac{\text{Peak Height}}{\text{Amplitude of the Background Current Noise}} = 2$$

Chemicals

Matheson furnished mixtures containing 350 ppm of nitrogen dioxide in nitrogen, and 319 ppm of nitric oxide in nitrogen. They also supplied cylinders of nitrogen, nitrogen dioxide, dinitrogen trioxide and carbon dioxide.

Methyl nitrate was furnished by K & K Laboratories.

Ohio Chemical Pacific Company provided a cylinder of nitrous oxide.

Nitromethane, acetaldehyde, biacetyl, acetic acid and methyl acetate were furnished by Eastman Organic Chemicals.

Matheson, Coleman and Bell supplied formamide and acetone.

Experimental Procedure

The procedure for the calibration of the electron-capture detector for nitrogen dioxide is presented, but the same technique was followed for the calibration of the other compounds.

The reactor was evacuated below a pressure of 0.005 mm Hg. A partial pressure of nitrogen dioxide of approximately 75 mm Hg was added to the reactor from a mix tank or directly from a gas cylinder. Nitrogen was added to the reactor to bring the total pressure of the reactor to approximately one atmosphere. The mixture in the reactor was ten percent nitrogen dioxide and ninety percent nitro-

gen. Partial evacuations of the reactor to a pressure of 75 mm Hg, and subsequent additions of nitrogen to bring the pressure of the reactor to one atmosphere, were used to dilute the mixture of nitrogen dioxide in nitrogen. Five dilutions were required to obtain a mixture containing 50 ppm of nitrogen dioxide in nitrogen at room temperature and a total pressure of one atmosphere.

After forming the initial calibration mixture, the chromatograph was conditioned by injection of samples of nitrogen dioxide and hydrocarbons from the standard tank into the chromatograph columns. Several 0.5 cc samples from the standard tank were analyzed at ten minute intervals until reproducible peak heights (electron-capture) and peak areas (flame-ionization) were obtained.

When the detectors were standardized, the calibration mixture was analyzed. Three to seven samples were required at each concentration. Samples were taken at ten minute intervals. Lower concentrations of nitrogen dioxide in nitrogen were obtained by partial evacuatuon of the reactor followed by the addition of nitrogen to bring the total pressure of the reactor back to one atmosphere. A normal calibration consisted of fifteen to twenty concentrations below 40 ppm of nitrogen dioxide in nitrogen, and lasted six to eight hours.

Results

Calibration curves were obtained for the electron-capture detector for nitrogen dioxide (Figure D.1), carbon dioxide (Figure D.2), methyl nitrite (Figure D.3), and nitromethane (Figure D.4). The calibration curve for the hydrogen flame-ionization detector was also determined for acetaldehyde (Figure D.5).

The detection limits for the electron-capture detector are presented in Table D.1. Table D.2 summarizes the detection limits for the hydrogen flame-ionization detector.

Conclusions

The electron-capture detector is very sensitive to compounds with high affinities for free electrons. The response of the detector is non-linear since only a small portion of the calibration curves can be approximated by a straight line. Therefore, the electron-capture detector is suitable for quantitative analysis only in limited concentration ranges.

The hydrogen flame-ionization detector is excellent for quantitative determination of hydrocarbons because of its high sensitivity. The response of the detector is linear over a large range of concentrations.

Table D.1 Detection limits for the electron-capture detector.

Compound	Detection Limit, ppm
nitrogen dioxide	0.1
carbon dioxide	0.6
methyl nitrite	0.1
nitromethane	0.3
nitrogen	0.3
oxygen	9.8
acetaldehyde	0.6
nitrous oxide	0.1
methyl nitrate	0.4

Table D.2 Detection limits for the hydrogen flame-ionization detector.

Compound	Detection Limit, ppm
acetaldehyde	0.4
methyl nitrite	1.8
nitromethane	2.0
methane	0.3
ethane	0.3
acetone	0.5
biacetyl	0.8
glyoxal	0.8
acetic acid	1.1
methyl acetate	0.9
formamide	1.5
formaldoxime	1.5

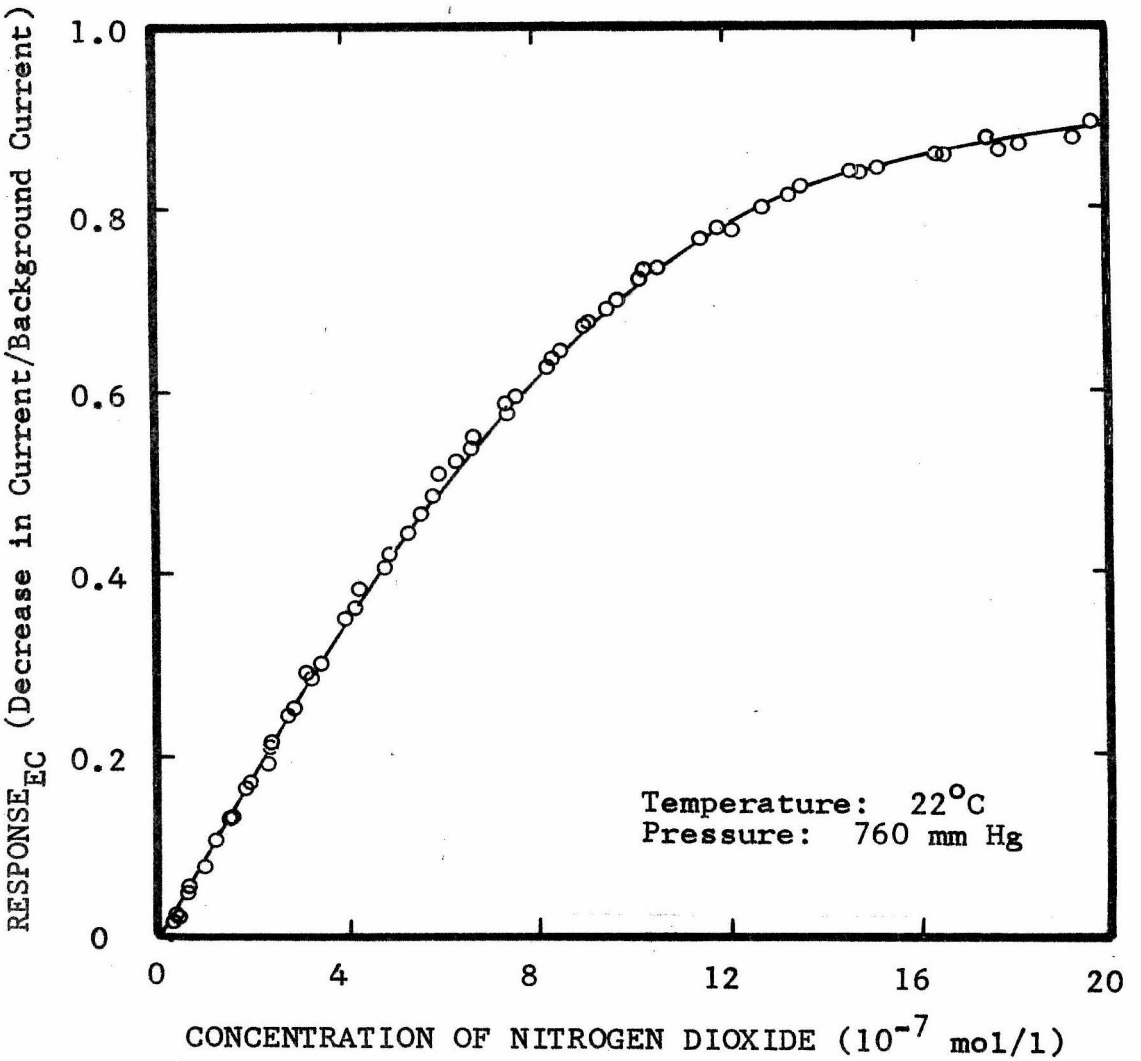


Figure D.1 Calibration curve for nitrogen dioxide for the electron-capture detector.

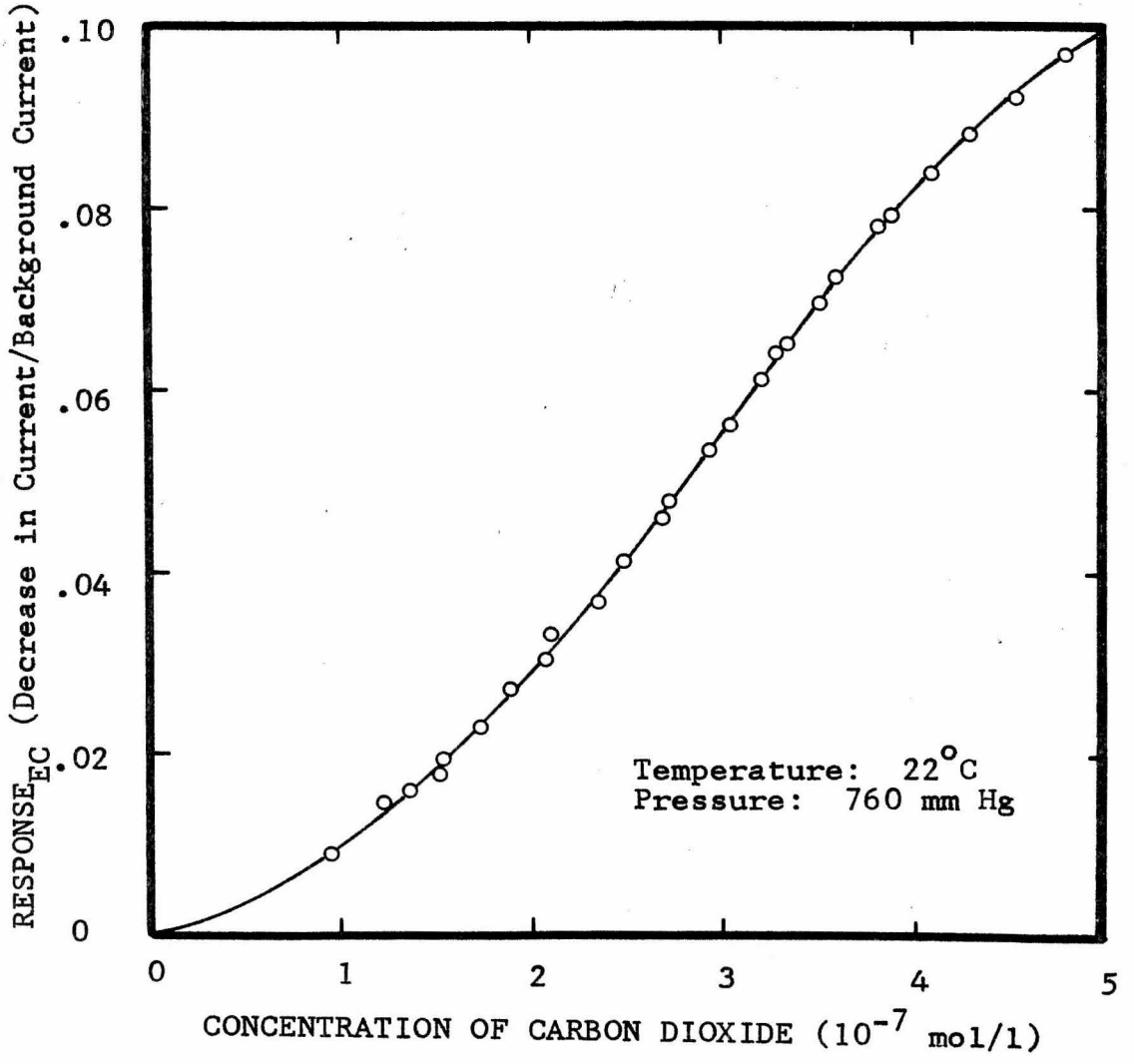


Figure D.2 Calibration curve for carbon dioxide for the electron-capture detector.

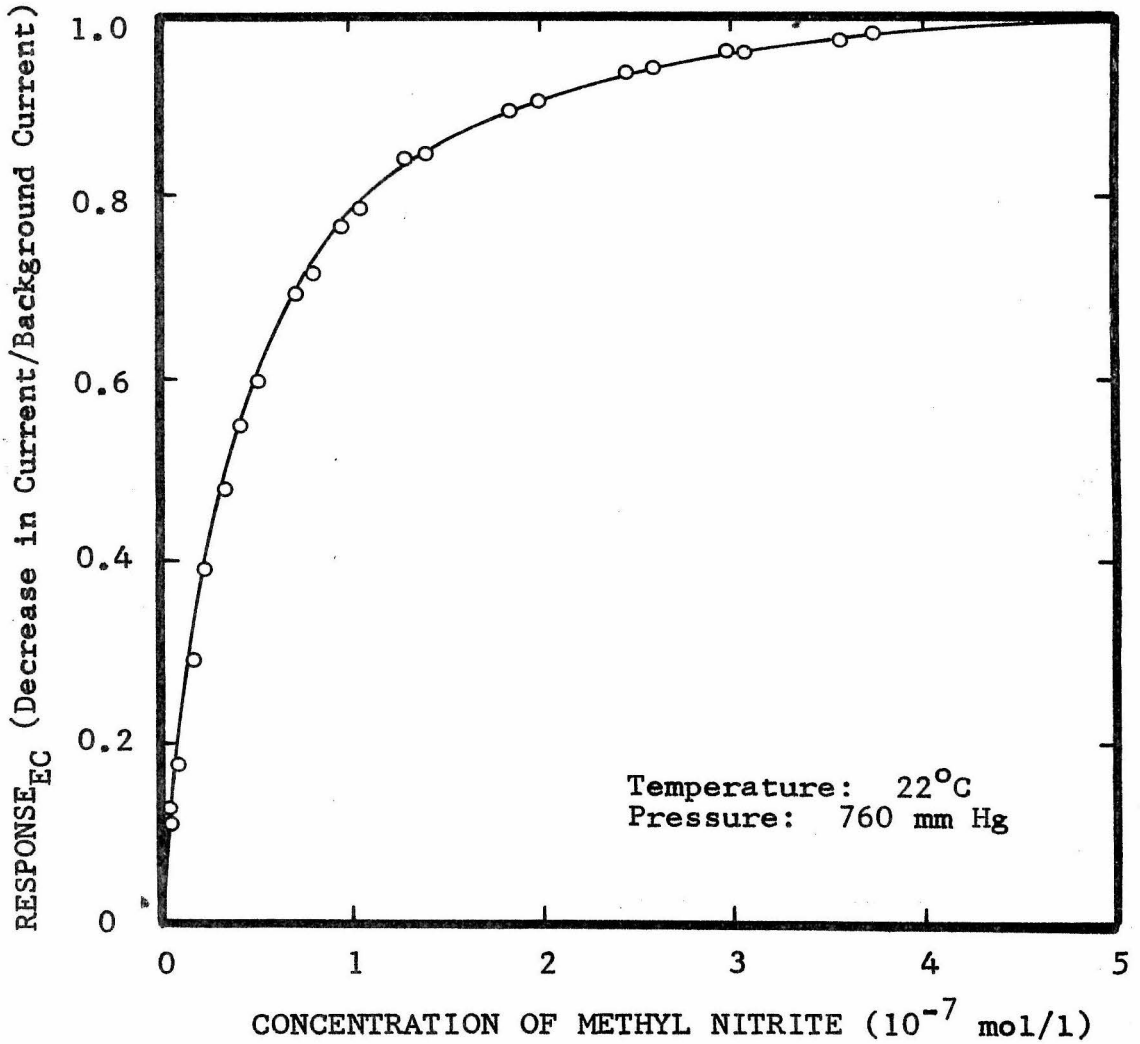


Figure D.3 Calibration curve for methyl nitrite for the electron-capture detector.

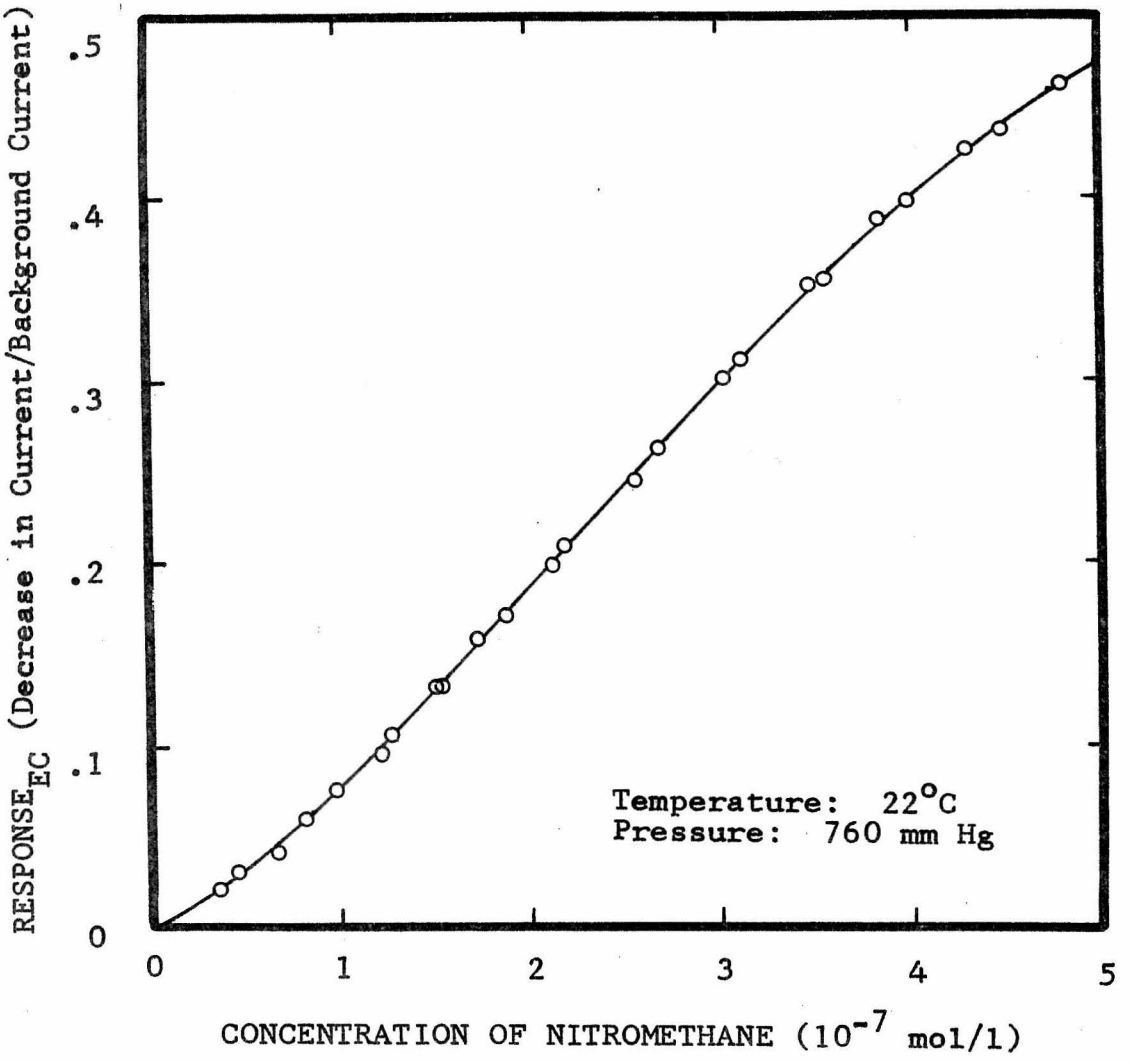


Figure D. 4 Calibration curve for nitromethane for the electron-capture detector.

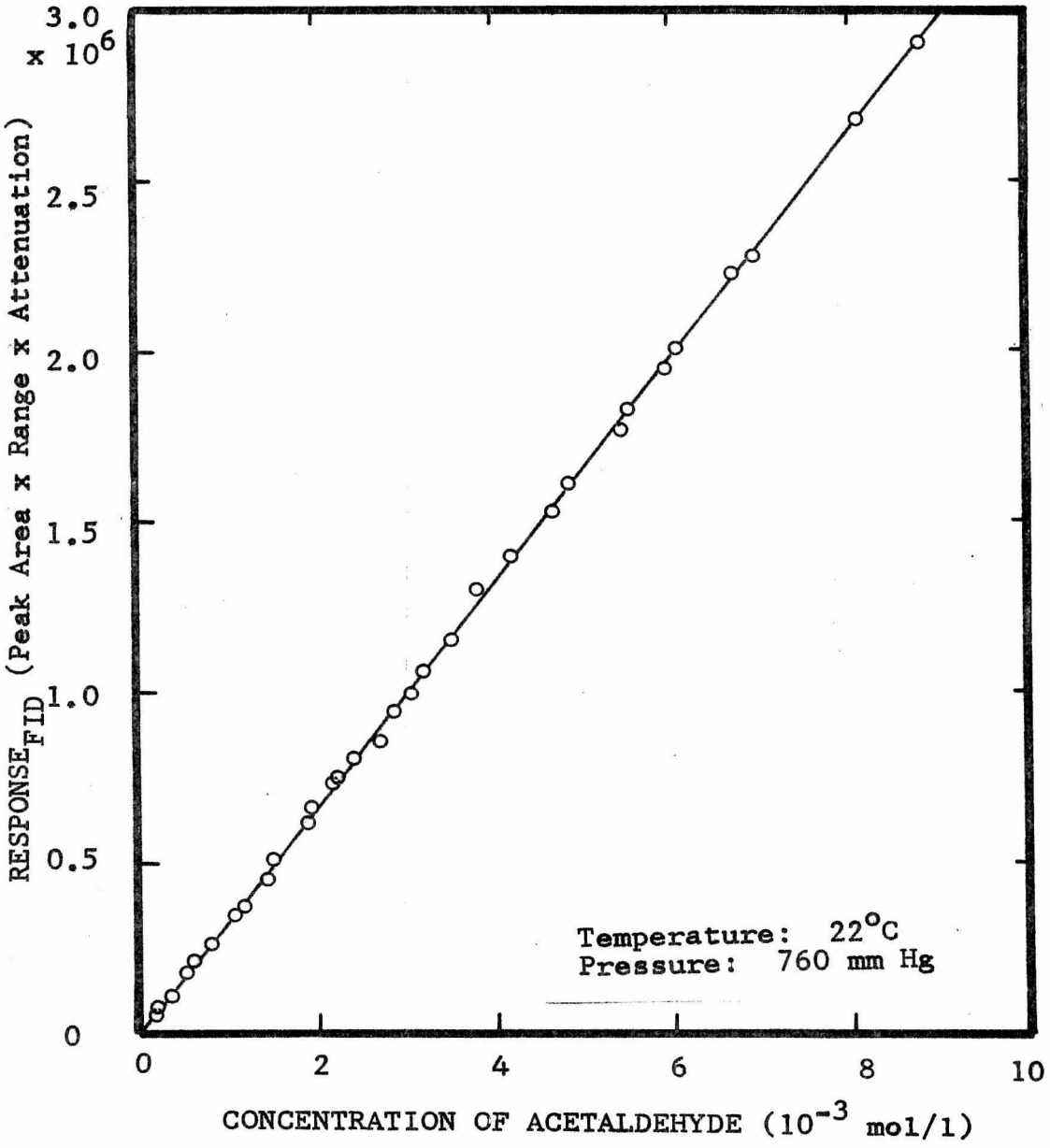


Figure D.5 Calibration curve for acetaldehyde for the hydrogen flame-ionization detector.

PROPOSITIONS

PROPOSITION I

The exact structure of dinitrogen trioxide, N_2O_3, has not been determined experimentally. A structure for dinitrogen trioxide can be proposed by qualitatively considering that the molecule is composed of a nitric oxide molecule and a nitrogen dioxide molecule. An explicit molecular orbital representation of dinitrogen trioxide is developed which is consistent with a planar nitronitroso-, $ON\text{-}NO_2$, structure.

Introduction

Pure dinitrogen trioxide, N_2O_3, exists only as a solid. As a liquid it is partially dissociated to nitric oxide, nitrogen dioxide and dinitrogen tetroxide. It is almost entirely dissociated in the gas phase[14].

Direct evidence of the molecular structure of dinitrogen trioxide is not available. The results of the x-ray study[19] of the solid (m.p. ca -103°C) at -115°C were inconclusive. The liquid (b.p. ca 3.5°C) is diamagnetic and non-conducting[23], and is less likely to ionize than dinitrogen tetroxide[2]. D'Or and Tarte[9] studied the infrared spectrum of gaseous dinitrogen tetroxide (at room temperature in the presence of the dissociation products, nitric oxide and nitrogen dioxide, and in the presence of nitrous acid) and reported that dinitrogen tetroxide could not be assigned a nitrito, O-N-O-N-O, structure. They concluded that the fundamental frequencies of a nitronitroso-structure, $ON-NO_2$, could be chosen to fit the corresponding frequencies of nitric oxide, nitrogen dioxide and dinitrogen trioxide. The available spectroscopic data of Hisatsume and Rhee[12] appear consistent with the nitro-nitroso-structure for dinitrogen trioxide.

The low heat of dissociation of dinitrogen trioxide suggests a weak nitrogen-nitrogen bond in the nitronitroso-structure, $ON---NO_2$. The dissociation energy of dinitrogen trioxide is 10.3 kcal/mole, which is close to the heat of

dissociation of 12.875 kcal/mole for dinitrogen tetroxide, N_2O_4. Dinitrogen tetroxide possesses a weak nitrogen-nitrogen bond, O_2N---N_2O. The dissociation energy of a normal nitrogen-nitrogen single bond, such as in hydrazine (H_2N-NH_2), is about 60 kcal/mole. Therefore, dinitrogen trioxide, $ON-NO_2$, should have a weak N-N bond similar to dinitrogen tetroxide, O_2N-NO_2.

Coulsen and Duchesne[7] and Smith and Hedberg[21] contend that the N-N bond in N_2O_4 is formed by pi-bonding, with no resultant sigma-bonding. The pi-bonding would account for the planarity of dinitrogen tetroxide. Chalvet and Daudel[5] calculated a N-N bond order of 1.164 for N_2O_4 considering a combination sigma- and pi-bond. This bond order is obviously too high, since the N-N bond distance in O_2N-NO_2 is greater than a single N-N bond.

Supporters of a nitronitroso-structure, $ON-NO_2$, for dinitrogen trioxide include Wieland[23], Ingold and Ingold[13], Walsh[22], Addison and Lewis[1], Coulsen and Duchesne[7], and Cartmell and Fowles[4].

In contrast, Sidgwick[20] prefers a nitrito, O-N-O-N-O structure for dinitrogen trioxide based on the results of Leifer[15]. Leifer observed a rapid exchange of N^{14} of nitric oxide with N^{15} of nitrogen dioxide:

$$N^{15}O_2 + N^{14}O \rightleftharpoons O-N^{14}-O-N^{15}-O \rightleftharpoons N^{14}O_2 + N^{15}O$$

He concluded that the two nitrogen atoms in dinitrogen trioxide were equivalent, therefore, he supported the nitrito-structure.

Theory

Nitric oxide, NO, is the most stable of the odd-electron molecules. The bond distance[8] of 1.151 Å is between the bond length of a N-O double bond, 1.20 Å, and the bond length of a N-O triple bond, 1.06 Å. The molecular orbital description[3] of the nitric oxide molecule (taking the x-axis along the line of the centers) is:

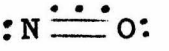
$$(2s_N)^2(2s_O)^2(\sigma_{N/2px-O/2px})^2(\pi_{N/2py-O/2py})^2(\pi_{N/2pz-O/2pz})^3$$

or

$$(2s_N)^2(2s_O)^2(\sigma_{N/2px-O/2px})^2(\pi_{N/2pz-O/2pz})^2(\pi_{N/2py-O/2py})^3$$

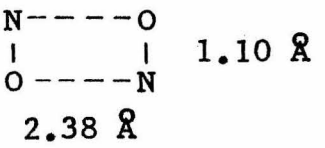
Four electrons in nitrogen are non-bonding, $(1s_N)^2(2s_N)^2$, and four electrons in oxygen are non-bonding, $(1s_O)^2(2s_O)^2$. The nitric oxide molecule has one sigma-bond, $(\sigma_{N/2px-O/2px})^2$, and one pi-bond, either $(\pi_{N/2py-O/2py})^2$ or $(\pi_{N/2pz-O/2pz})^2$. The nitric oxide molecule also possesses a three-electron bond, either $(\pi_{N/2pz-O/2pz})^3$ or $(\pi_{N/2py-O/2py})^3$. The three-electron bond is a half pi-bond since the extra electron is in an anti-bonding pi-orbital.

Pauling[18] assigned the structure



to the nitric oxide molecule. This structure involves a double bond and a three-electron bond between oxygen and nitrogen. Pauling concluded that of the four valence orbitals of each atom, one orbital contained the non-bonding unshared pair of electrons, two orbitals were used for the double bond, and one orbital was employed for the three-electron bond.

When nitric oxide dimerizes, it forms a head-to-tail rectangle. The long side is 2.38 Å and the short side is 1.10 Å.

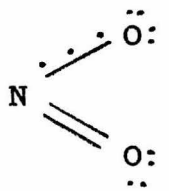


Nitrogen dioxide, NO_2, is also an odd-electron molecule. The N-O distance[17] is 1.18 Å and the O-N-O bond angle is 134°. The molecular orbital description[10] of nitrogen dioxide is:

$(1s_N)^2(1s_{O'})^2(1s_{O''})^2(2s_{O'})^2(2s_{O''})^2(2p_{z/N})^2(2p_{x/O'})^2(2p_{y/O''})^2$
$(\sigma_{N/sp2/xy\text{-}O'/2py})^2(\sigma_{N/sp2/xy\text{-}O''/2px})^2(\pi_{O'/2pz\text{-}N/2pz\text{-}O''/2pz})^2$
$(\sigma_{N/sp2/xy})^1$

The electronic configuration of the ground state yields two sigma-bonds, $(\sigma_{N/sp2/xy\text{-}O'/2py})^2$ and $(\sigma_{N/sp2/xy\text{-}O''/2px})^2$. In this description, the pi-bond is distributed over the three atoms, $(\pi_{O'/2pz\text{-}N/2pz\text{-}O''/2pz})^2$, and the odd-electron is in a non-bonding sigma-orbital, $(\sigma_{N/sp2/xy})^1$. Gray[10] states that electron spin resonance measurements have confirmed that the unpaired electron is in a sigma-orbital in the ground state of nitrogen dioxide.

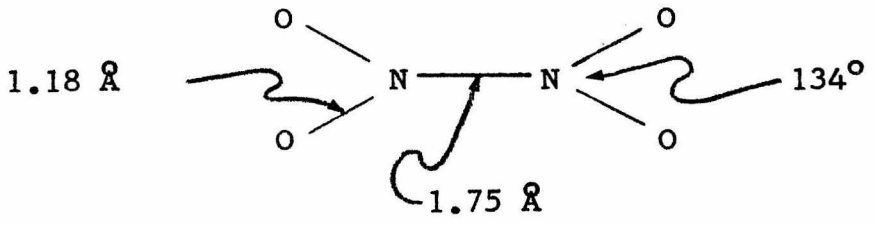
Pauling[18] assigned the structure



to the nitrogen dioxide molecule. In this structure, one oxygen is bonded to nitrogen by a double bond, and the other oxygen is bonded to nitrogen by a single bond and a three-electron bond.

Nitrogen dioxide dimerizes to form dinitrogen tetroxide, N_2O_4. The N-N bond length is 1.75 Å and the N-O bond length is 1.18 Å. The O-N-O bond angle is 134°. The mole-

cule is planar due to the slight conjugation of the pi-bonds. The structure is:



Discussion

The dinitrogen trioxide molecule can be considered as consisting of a nitric oxide molecule and a nitrogen dioxide molecule. A structure for dinitrogen trioxide can be proposed employing this technique for a molecular orbital approach and a valence bond method.

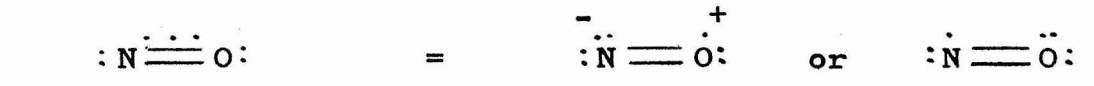
Considering the molecular orbital treatment, the N-N bond in N_2O_3 would be formed from the ($\pi_{N/2pz-O/2pz}$) orbital in nitric oxide, and the ($\pi_{N/2pz-O'/2pz-O''/2pz}$) orbital in nitrogen dioxide. Sigma-character would be introduced in the N-N bond in N_2O_3 from the ($\sigma_{N/sp2/xy}$) orbital in nitrogen dioxide and the ($\pi_{N/2pz-O/2pz}$) orbital in nitric oxide. The N-O bond lenth and the O-N-O bond angle in the nitro-group whould be the same as in nitrogen dioxide, 1.18 Å bond length and 134° bond angle. The N-O bond length in the nitroso-group should be the same as in nitric oxide, 1.15 Å. The N-N bond length in N_2O_3

should be greater than the N-N bond length in N_2O_4 because (1)the dinitrogen tetroxide molecule is symmetrical, (2) both nitrogen dioxide molecules in dinitrogen tetroxide have ($\sigma_{N/sp2/xy}$) orbital available for N-N bonding, and (3) the dinitrogen tetroxide molecule is stabilized by spreading the two pi-bonds over the entire molecule.

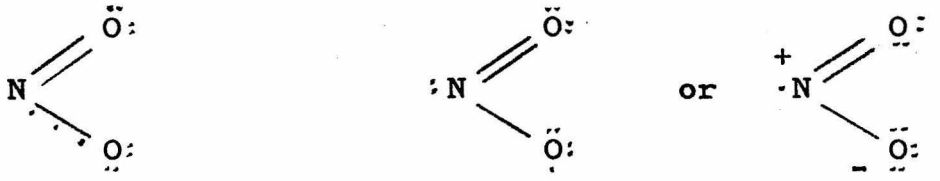
Jolly[14] estimated a N-N bond length of 2.08 Å for dinitrogen trioxide based on spectroscopic data. This value is reasonable since it is greater than the 1.75 Å N-N bond length in N_2O_4, but less than the 2.38 Å bond length for N-O in the N_2O_2 dimer.

The N_2O_3 molecule should be planar considering the overlapping orbitals between nitric oxide and nitrogen dioxide. Therefore, the N-N bond in dinitrogen trioxide should be less than a normal single bond because the electrons are not fully available for nitrogen-nitrogen bonding but are involved in N-O bonding in the individual NO and NO_2 groups. The N_2O_3 molecule should be planar due to the slight pi-bond character of the N-N bond.

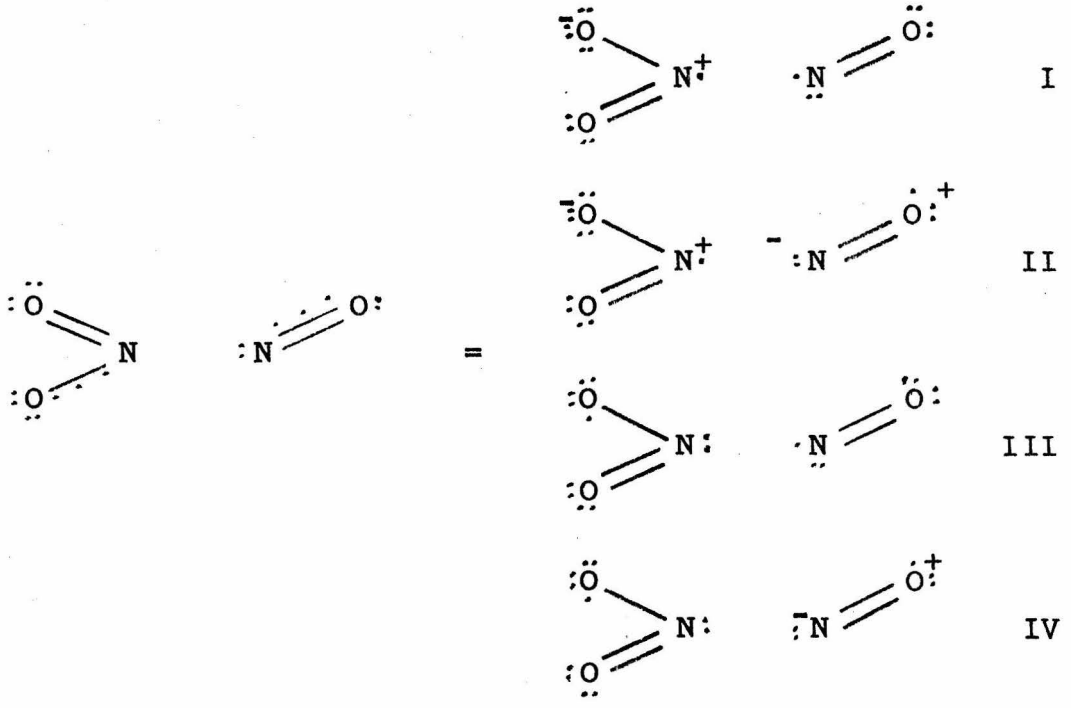
Valence bond theory can also be employed to explain the structure of dinitrogen trioxide. The nitric oxide molecule can be represented as



The nitrogen dioxide molecule can be represented as



The combination of a molecule of nitric oxide and a molecule of nitrogen dioxide to form a molecule of dinitrogen trioxide yields:



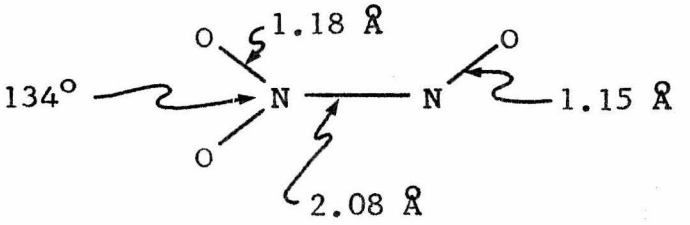
Structure I has a N-N single bond, two N-O double bonds, and one N-O single bond. Structures II and III have one N-N three-electron bond, one N-O double bond, one N-O 1½ bond, and one N-O 2½ bond. Structure IV has no formal N-N bond, one N-O 1½ bond, one N-O double bond,

and one N-O 2½ bond.

Valence bond theory predicts a N-N bond order of less than one since only one structure of the four has a formal N-N single bond. The valence bond approach also predicts a planar structure for dinitrogen trioxide since two of the four structures introduce pi-character into the N-N bond.

Conclusions

A structure for dinitrogen trioxide can be proposed by considering that the molecule is composed of a nitric oxide molecule and a nitrogen dioxide molecule. A planar nitronitroso-structure, $ON\text{-}NO_2$, is postulated as the configuration of dinitrogen trioxide.



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PROPOSITION II

It is postulated that an argon-ionization detector can be operated with a pulse applied potential to expand the concentration range of linear response, improve the stability of the detector, and increase the reproducibility of the response.

The hydrogen flame-ionization detector is the standard instrument employed for the analysis of small concentrations of organic compounds by gas chromatography. A relatively high detection limit of 4 ppm of formaldehyde was obtained for the hydrogen flame-ionization detector. As a practical example of the pulse mode of operation, the argon ionization detector was optimized for formaldehyde. A detection limit of 0.4 ppm of formaldehyde was obtained with the argon-ionization detector operated with a pulse amplitude of 35 volts, a pulse period of 225 microseconds, and a pulse width of 20 volts. Therefore, a ten-fold increase in sensitivity for formaldehyde was obtained with the argon ionization detector operated in the pulse mode compared to the hydrogen flame-ionization detector. The pulse operation yielded stability and reproducibility for the argon-ionization detector, but the major problem remained the limited concentration range for linear response.

Introduction

The argon-ionization detector[1,2] was very popular in the early 1960's. The sensitivity of the detector was comparable to the flame-ionization detector. The major disadvantage of the argon-ionization detector was its extremely small and variable linear range of response.

The normal mode of operation for the argon-ionization detector was with a high dc potential, 100 to 300 volts. The object of this investigation was to determine if the pulse mode of operation for the argon-ionization detector improved (1)the stability of the background current, (2) the concentration range for linear response, and (3)the sensitivity of the detector.

The detection limit of the hydrogen flame-ionization detector for formaldehyde, HCHO, was found to be relatively high, 3.7 ppm. As a practical example, the response of the argon-ionization detector was studied to determine if a lower detection limit could be obtained.

Theory of the Argon-Ionization Detector

The absorption of radiation by gases produces ionization or excitation of the molecules. Excited, or metastable, atoms rapidly emit light and return to the ground state. Some metastable atoms exist long enough to collide with other molecules. The collisions may produce a trans-

fer of energy from the metastable atoms to the molecules of solute. With sufficient energy transfer, the solute molecules may ionize.

In the argon-ionization detector, many of the argon atoms are elevated to the first resonance level, about 11.7 ev. The excited atoms of argon have a relatively long half-life, 10^{-4} sec, and subsequent collisions of the metastable argon atoms with solute molecules can produce energy transfer. Compounds with ionization potentials below 11.7 ev would be ionized. If more energetic states of metastable argon existed, compounds with higher ionization potentials would also be ionized.

The basic equations for the argon-ionization detector are:

$$A + \beta^- \xrightarrow{15.7\ ev} A^+ + 2\ e^- \qquad (1)$$

$$A + e^- \xrightarrow{11.7\ ev} A^* + e^- \qquad (2)$$

$$A^* + C \longrightarrow A + C^+ + e^- \qquad (3)$$

$$A^* + S \longrightarrow A + S^+ + e^- \qquad (4)$$

where β^- is a beta-ray, A is a stable atom of argon, A* is a metastable argon atom, C is a molecule of contaminant, and S is a solute molecule.

Initially, some atoms of argon are ionized by beta-rays in reaction (1). The majority of the electrons in the detector produce metastable argon atoms by reaction (2). In reaction (3), the excited atoms of argon combine with molecules of contaminant (in the carrier gas) and produce positive ions and negative electrons. The metastable argon atoms also react with molecules of solute to produce positive ions and negative electrons, reaction (4). Reactions (1), (2) and (3) contribute to the background current of the argon-ionization detector, and reaction (4) is the response of the detector to the molecules of solute. Initiating electrons are regenerated by the chain reactions, therefore, the concentration of metastable argon is unaffected by collisions with solute molecules.

Physically, the argon-ionization detector is similar to the electron-capture detector. The detector is a cylindrical chamber with a diameter and length of one centimeter. The vessel contains a beta-ray source which creates a background current between 10^{-10} and 10^{-8} amperes. The detector is connected to a potential source, and the electrodes are connected to an instrument for measuring the resulting current.

The parameters affecting the response of the argon-ionization detector are (1)geometry of the detector, (2) beta-ray source, (3)temperature of the detector, (4)flow

rate of argon, (5)purity of the argon carrier gas, and (6)applied potential.

Experimental

The object of this investigation was to determine the optimum conditions for the pulse mode of operation of the argon-ionization detector. It was also desirable to obtain a detection limit below 1 ppm for formaldehyde by the detector.

A plane-parallel ionization detector designed by Morrison[3] was used in this study. The beta-ray source was tritium foil with an activity of 200 mc. The temperature of the detector was 190°C. High-purity dry argon was furnished by Linde. Impurities in the argon were removed in a cylinder with a length of one foot and an inside diameter of 1/2-inch. The tube was packed with 13X molecular sieve. The argon carrier gas was dried by passage through a coiled column which had been packed with 5A molecular sieve. The coiled column was four feet in length and was located in a dry-ice-acetone slurry.

The operation of the argon-ionization detector was investigated for pulse and dc potentials. The dc voltage ranged between 0.5 and 160 volts. Pulse operation was considered as a function of pulse amplitude (0.2 o 100 volts), period (10^{-2} to 10^{3} kc), and width (0.05 to 10^{4} microseconds).

Results and Discussion

A pulse mode of operation (pulse amplitude of 35 volts, pulse period of 225 microseconds, and a pulse width of 20 microseconds) for the argon-ionization detector was superior to the dc operation (100 volts). A background current of 8.1×10^{-8} amperes and a noise level of 4.3×10^{-12} amperes was obtained for the argon-ionization detector operated in the pulse mode. The corresponding background current of 1.8×10^{-8} amperes and noise level of 5.6×10^{-11} amperes was determined for the dc mode of operation.

Stability of the background current and reproducibility of the response of the detector were the major problems encountered. The purity of the argon carrier gas was the major factor affecting the stability of the detector. If the carrier gas was not dried, the noise level increased to 10^{-10} amperes, drift of the background current became a major problem, and the response of the detector was not reproducible. The same problems occurred when the sample valve leaked or teflon tubing was used in the flow system.

Conclusions

The detection limit of the argon-ionization detector (optimum conditions for the pulse mode of operation) for formaldehyde was 0.4 ppm. This compares to a detection limit of 3.7 ppm for the hydrogen flame-ionization detector. The response of the flame-ionization detector was

linear over the concentration range from 4 to 50 ppm of formaldehyde. In contrast, the response of the argon-ionization detector was non-linear in the same concentration range. The flame-ionization detector was more stable and gave better reproducibility than the argon-ionization detector.

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PROPOSITION III

It is proposed that the elementary thermal reactions in the gas phase between organic compounds and the oxides of nitrogen must be investigated before complex photochemical systems of nitric oxide-oxygen-nitrogen dioxide-hydrocarbons can be considered. A clear understanding of the thermal rate of reaction, reaction intermediates, and products of the reaction, is necessary in the formulation of the photochemistry of air pollution.

The effect of methane, ethane, propane and butane on the reaction between nitric oxide and oxygen was investigated at room temperature, in the gas phase, and at total pressures near one atmosphere. The elementary paraffins did not influence the quantitative conversion of nitric oxide to nitrogen dioxide. There were no measurable reactions between the paraffins and nitric oxide or nitrogen dioxide.

There was no measurable reaction between nitric oxide and ethylene. Nitric oxide was also oxidized by oxygen in the presence of ethylene. A complex series of heterogeneous reactions occurred which produced a broad spectrum of organic products. The reaction between ethylene and nitrogen dioxide was very complex, with non-volatile products being formed.

Introduction

At the present time, several crucial aspects of the problems of air pollution remain unsolved. The oxides of nitrogen and hydrocarbons are of principal interest in the chemistry of air pollution[4,6,10]. Nitric oxide, reactive hydrocarbons (olefins and alkyl benzenes), and oxygen are photochemically consumed in the atmosphere. The principal products of the photochemical reactions are nitrogen dioxide, oxidants (ozone and peroxyacetyl nitrate), and oxidation and nitration products of the organic compounds (formaldehyde, acetaldehyde, acrolein, PAN and alkyl nitrites)[1,9,10]. The reaction system is extremely complex, and in particular, the rapid conversion of nitric oxide to nitrogen dioxide is not clearly understood. The thermal reaction between nitric oxide and oxygen to produce nitrogen dioxide is too slow to account for the rapid rate of conversion of nitric oxide[2,6]. In the presence of reactive hydrocarbons, only fifty percent of the organic products have been identified in the photochemical conversion of nitric oxide to nitrogen dioxide[8].

The object of this investigation was to determine the effect of elementary hydrocarbons (methane, ethane, propane, butane and ethylene) on the air oxidation of NO. The thermal reaction in the gas phase was considered at room temperature and a total pressure of one atmosphere.

Nitric Oxide-Oxygen Reaction

The thermal reaction between nitric oxide and oxygen to form nitrogen dioxide has been extensively studied:

$$2\ NO + O_2 \longrightarrow 2\ NO_2 \qquad (1)$$

Several authors[4,7,9] have summarized the results of the thermal oxidation of nitric oxide. The majority of the investigators observed third-order kinetics for the reaction between nitric oxide and oxygen. The initial rate of disappearance of nitric oxide was second-order in nitric oxide and first-order in oxygen. An initial third-order rate constant of approximately 1.4×10^4 $l.^2 mole^{-2} sec^{-1}$ was reported at 25°C. Several studies observed an increase in the third-order rate constant as the reaction proceeded. Mechanisms were proposed incorporating NO_3, $(NO)_2$, N_2O_3 and N_2O_5 as intermediates. All investigators reported a small negative temperature coefficient for the initial third-order rate constant.

Altshuller, Cohen and Kopczynski[2] reported that the photochemical oxidation of nitric oxide in the presence of certain hydrocarbons (olefins and alkyl benzenes) was faster than the corresponding thermal oxidation of nitric oxide by oxygen. Therefore, it would be of interest to determine the effect of hydrocarbons on the thermal oxida-

tion of nitric oxide. Considerable experience had been acquired in a previous study of the air oxidation of ppm concentrations of nitric oxide[7]. In order to determine the reactivity of elementary hydrocarbons, paraffins (methane, ethane, propane and butane) and an olefin (ethylene) were introduced as initial reactants in the nitric oxide-oxygen system. The thermal reactions between nitric oxide and the hydrocarbons, nitrogen dioxide and the hydrocarbons, and the effect of the hydrocarbons on the thermal oxidation of nitric oxide were investigated.

Hydrocarbon-Oxides of Nitrogen Reactions

Very little information was found in the literature concerning the influence of hydrocarbons on the thermal reaction between nitric oxide and oxygen at room temperature. Limited data were available regarding the thermal reactions between hydrocarbons and the oxides of nitrogen at low temperatures.

Altshuller, Cohen and Kopczynski[2] studied the thermal oxidation of nitric oxide, and the photochemical oxidation of nitric oxide in the presence of olefins and aromatic hydrocarbons. When an olefin, nitric oxide and oxygen were exposed to ultraviolet light, a rapid photochemical oxidation of nitric oxide occurred. They found that a number of aromatic hydrocarbons (toluene, p-xylene, m-xylene, o-xylene, mesitylene and isopropyl benzene) par-

ticipated as effectively as olefins (ethylene, propylene and isobutene) in photochemical oxidation reactions in the atmosphere. Altshuller, et. al., observed that the photochemical oxidation of nitric oxide in the presence of olefins or aromatic hydrocarbons was much more rapid than the corresponding thermal oxidation of nitric oxide by oxygen.

Coltrell and Graham[5] investigated the thermal reaction in the gas phase between ethylene and nitrogen dioxide. They investigated the reaction in the temperature range between 160 and 290°C, and at total pressures from 30 to 120 mm Hg. The products of the reaction between ethylene and nitrogen dioxide were nitric oxide, carbon dioxide, carbon monoxide, a liquid with a high boiling point, and a dark solid. The addition of nitric oxide did not affect the rate of reaction of nitrogen dioxide, the rate of formation of the products, or the distribution of the products.

Takeuchi[11] studied the reaction of ethylene and nitrogen dioxide in the gas phase at room temperature. The products of the reaction were nitric oxide, carbon dioxide, formaldehyde, acetaldehyde, glyoxal, formic acid, acetic acid, oxalic acid, water, nitrobenzene, nitrosoethylene and nitroethylene. Irradiation by mercury lamps increased the consumption of nitrogen dioxide and accelerated the rate of disappearance of nitrogen dioxide. Formaldehyde and the polymer form of formaldehyde were produced, but

carbon dioxide and glyoxal were not produced in the photochemical reaction.

Takeuchi found that the addition of oxygen did not alter the products of the reaction, but retarded the rate of consumption of nitrogen dioxide. The addition of oxygen increased the production of carbon dioxide, formaldehyde, glyoxal and the acids. The addition of glass wool to the reactor did not affect the rate of reaction of nitrogen dioxide.

Altshuller, Klosterman, Leach, Hindawi and Sigsby[3] investigated the photochemical reactions between the oxides of nitrogen and various organic compounds. They also considered the biological effects of the products of the photochemical reactions. Paraffins, acetylene and benzene did not react photochemically with nitric oxide or nitrogen dioxide. Olefins, aldehydes and aromatics (except benzene) participated in photo-chemical reactions with the oxides of nitrogen. The photochemical products of the atmospheric reactions created oxidants, significant eye irritation and measurable plant damage.

All the olefins investigated (ethylene, 1-butene and 1,3-butadiene) photochemically reacted with nitric oxide. Formaldehyde was the principal product of the reaction between ethylene and nitric oxide. The photochemical products of the reaction between 1-butene and nitric oxide

were ethane, ethylene, acetaldehyde, methyl nitrate, peroxyacyl nitrate and peroxyprionyl nitrate. Formaldehyde, acrolein and peroxyacetyl nitrate were the additional products of the photochemical reaction between 1,3-butadiene and nitric oxide.

Experimental Method

The object of the experiment was to determine the effects of paraffins and olefins on the air oxidation of nitric oxide. Morrison[7] had previously studied the thermal conversion of ppm concentrations of nitric oxide to nitrogen dioxide in the gas phase at room temperature and at total pressures near one atmosphere.

The thermal reactions between the oxides of nitrogen and various hydrocarbons were also part of the investigation. Methane, ethane, propane and butane were the paraffins considered. Ethylene was the only olefin studied. Each of the hydrocarbons were tried with (1)nitric oxide, (2)nitrogen dioxide, and (3)nitric oxide and oxygen.

Experimental Apparatus

Oxygen, nitrogen, nitric oxide and nitrogen dioxide were furnished by Matheson. Phillips Petroleum Company supplied methane, ethane, propane, butane and ethylene. Oxygen and nitrogen were dried before use in the equipment. The concentrations of the oxides of nitrogen were determined by the phenol-disulfonic acid method (ASTM D

1608-60).

The constant-volume batch reactor was a borosilicate glass vessel with an outside diameter of six inches, a length of twelve inches, and a volume of approximately three liters. Temperature control was maintained by a Fisher thermoregulator located in the air bath surrounding the reactor.

Gas chromatography was used for the analysis of gaseous products and reactants. A 20-foot column of 10% SF-96 on Teflon 6 was used to separate inorganic gases, oxidized organic compounds and nitrated constituents. An electron-capture detector was employed for the detection of these components. Poropak columns were used for the separation of organic compounds in conjunction with their analysis by a hydrogen flame-ionization detector.

Experimental Procedure

In a test, the reactor was evacuated below a pressure of 0.005 mm Hg. Nitric oxide (or nitrogen dioxide) was added to the reactor, followed by the addition of nitrogen to the reactor. The desired partial pressure of nitric oxide (or nitrogen) was obtained by partial evacuation of the reactor and subsequent addition of nitrogen. The pressure in the reactor was determined by a mercury manometer. A cathetometer was used to read the level of the mercury. No pressure change less than 50 mm Hg was used, and a maxi-

mum of three dilutions were required. After the initial concentration of nitric oxide (or nitrogen dioxide) was obtained, the chromatograph was conditioned with samples of nitrogen dioxide and organic compounds. A hydrocarbon (methane, ethane, propane, butane or ethylene) was added to the reactor and the timer started. Samples were taken from the reactor and analyzed with the chromatograph.

Next, the effect of paraffins and olefins on the air oxidation of nitric oxide was investigated. In these tests, ppm concentrations of nitric oxide were oxidized by oxygen to nitrogen dioxide. The concentration-time data for the oxidation of nitric oxide were compared to the results predicted by Morrison[7]. A mixture of 30 ppm of nitric oxide in nitrogen (80%) and oxygen (20%) was quantitatively converted to nitrogen dioxide. With the same initial conditions (temperature, total pressure of the reaction, partial pressure of nitric oxide, partial pressure of oxygen), individual hydrocarbons were added as initial reactants. Four tests for the thermal air oxidation of nitric oxide were made with each hydrocarbon. The initial partial pressures of the hydrocarbons varied between 100 ppm and 10% of the total reactor pressure. In an oxidation test, nitric oxide and nitrogen were added to the reactor. The chromatograph was conditioned after the addition of the initial quantity of hydrocarbon. When oxygen was added to the reactor, the timer was started,

and samples were taken from the reactor and analyzed.

Results

There were no measurable reactions between the paraffins and nitric oxide or nitrogen dioxide. In the gas phase, at 25°C, and at total pressures near one atmosphere, methane, ethane, propane and butane did not thermally react with the oxides of nitrogen. The results of the air oxidation of ppm concentrations of nitric oxide agreed with the concentration-time results predicted by Morrison. Methane, ethane, propane and butane did not affect the rate of reaction of nitric oxide, or the quantitative conversion of nitric oxide to nitrogen dioxide.

There was no measurable reaction between ethylene and nitric oxide at 25°C. There was a rapid reaction in the gas phase between nitrogen dioxide and ethylene. The products that were identified included nitric oxide, carbon dioxide, formaldehyde, acetaldehyde, formic acid, acetic acid, acetone and nitrobenzene. Five peaks on the chromatograms were not identified. In addition, a white polymeric substance formed on the walls of the reactor and droplets of a clear liquid were observed during the reaction.

The addition of ethylene significantly altered the air oxidation of nitric oxide. The rate of formation of nitrogen dioxide was reduced, and nitric oxide was not

quantitatively converted to nitrogen dioxide. The products that were isolated included carbon dioxide, carbon monoxide, water, formaldehyde, acetic acid, acetaldehyde, formic acid and acetone. Two additional unknown peaks were observed on the chromatograms. The following non-volatile products were observed in the reactor: (1)a dark brown oily residue, (2)black flakes, (3)white crystals, (4)a yellowish liquid, and (5)milky-white liquid droplets. The reactions were obviously heterogeneous and extremely complex. The present chromatograph was not equiped to analyze the spectrum of products of the reactions.

Discussion

The paraffins (methane, ethane, propane and butane) did not thermally react with nitric oxide or nitrogen dioxide at 25°C. The paraffins also did not affect the air oxidation of ppm concentrations of nitric oxide at room temperature. Altshuller, et. al.[3], also found that paraffins did not react thermally or photochemically with nitric oxide at low temperatures.

In the reaction between ethylene and nitrogen dioxide, Takeuchi[11] identified nitric oxide, formaldehyde, acetaldehyde, carbon dioxide, formic acid, acetic acid, oxalic acid, glyoxal, water and nitrobenzene as products at room temperature. He concluded that the primary reaction intermediate was either ethylene oxide or acetaldehyde. Since

the thermal reaction between nitrogen dioxide and acetaldehyde produced carbon dioxide, glyoxal and acetic acid, and the reaction between ethylene oxide and nitrogen dioxide produced no volatile organic compounds but a nitrogen compound with a high boiling point, Takeuchi concluded that acetaldehyde was the principal reaction intermediate. He proposed the following reaction mechanism:

$$C_2H_4 + NO_2 \longrightarrow CH_3CHO + NO \quad (2)$$

$$CH_3CHO + NO_2 \longrightarrow CH_3CO_2H + NO \quad (3)$$

$$CH_3CHO + N_2O_4 \longrightarrow (CHO)_2 + H_2O + 2NO \quad (4)$$

$$(CHO)_2 + NO_2 \longrightarrow C(OH)COOH + NO \quad (5)$$

$$(CHO)_2 + N_2O_4 \longrightarrow (COOH)_2 + 2\,NO \quad (6)$$

$$(CHO)_2 + NO_2 \longrightarrow HCHO + CO_2 + NO \quad (7)$$

$$HCHO + NO_2 \longrightarrow HCO_2H + NO \quad (8)$$

$$HCO_2H + NO_2 \longrightarrow CO_2 + H_2O + NO \quad (9)$$

$$C(OH)COOH + NO_2 \longrightarrow (COOH)_2 + NO \quad (10)$$

$$CH_3CHO + NO_2 \longrightarrow 2\,HCHO + NO \quad (11)$$

$$n\ HCHO \longrightarrow (HCHO)_n \quad (12)$$

$$C_2H_4 + NO_2 \longrightarrow C_2H_3 + HNO_2 \quad (13)$$

$$C_2H_3 + NO \longrightarrow C_2H_3NO \quad (14)$$

$$C_2H_3NO + NO_2 \longrightarrow C_2H_3NO_2 + NO \quad (15)$$

$$2\ HNO_2 \longrightarrow NO_2 + NO + H_2O \quad (16)$$

$$C_2H_3 + NO_2 \longrightarrow C_2H_2 + HNO_2 \quad (17)$$

$$C_2H_2 + N_2O_4 \longrightarrow (CHO)_2 + 2\ NO \quad (18)$$

In this experiment, there was a rapid thermal reaction between ethylene and nitrogen dioxide, but no reaction between nitric oxide and ethylene. A broad spectrum of oxidized and nitrated products were observed for the reaction between ethylene and nitrogen dioxide at room temperature. The reactions involved in the ethylene-nitrogen dioxide system were very complex. Interpretation of the reaction between ethylene and nitrogen dioxide would require extensive information concerning the secondary reactions of the oxides of nitrogen and organic intermediate products.

The results of this investigation showed that ethylene reduced the production of nitrogen dioxide in the air oxidation of ppm concentrations of nitric oxide. The products of the nitric oxide-oxygen-ethylene system were more complex than the products of the nitrogen dioxide-ethylene system. Initially, nitric oxide was oxidized by oxygen to form nitrogen dioxide. The nitrogen dioxide reacted with ethylene. The products of the reaction between nitrogen dioxide and ethylene reacted with nitrogen dioxide

and with oxygen. Therefore, the rate of formation of nitrogen dioxide in the reaction between nitric oxide and oxygen was faster with no ethylene present. The rate of formation of nitrogen dioxide decreased with ethylene present because nitrogen dioxide was consumed by ethylene and by reactions with secondary products.

Conclusions

The thermal oxidation of ppm concentrations of nitric oxide was not affected by methane, ethane, propane or butane. There were no measurable reactions between the paraffins and nitric oxide or nitrogen dioxide.

There was no reaction between nitric oxide and ethylene. The reaction between ethylene and nitrogen dioxide was very complex, with non-volatile products being formed. The nitric oxide-oxygen-ethylene system produced a broad spectrum of oxidized and nitrated organic products.

A systematic investigation of the reactions between elementary organic compounds and nitric oxide and nitrogen dioxide is necessary. The secondary products of the complex reactions must be isolated and studied separately. The reactions between the oxides of nitrogen and hydrocarbons should be considered before photochemical reactions are studied and before oxygen is added as an initial reactant.

Table 1. Initial conditions for the reactions between various hydrocarbons and the oxides of nitrogen

Hydrocarbon	Hydrocarbon Pressure (mm Hg)	Nitrogen Oxide	Nitrogen Oxide Pressure (mm Hg)	Temperature (°C)
methane	10.2	nitric oxide	26.7	25.1
methane	31.3	nitric oxide	11.7	25.0
methane	9.7	nitrogen dioxide	33.1	25.0
methane	28.9	nitrogen dioxide	12.2	25.0
methane	41.2	nitric oxide	43.7	25.2
methane	39.9	nitrogen dioxide	41.1	25.1
ethane	14.6	nitric oxide	16.7	25.0
ethane	16.1	nitrogen dioxide	16.6	25.0
propane	18.9	nitric oxide	16.1	25.1
propane	17.4	nitrogen dioxide	16.9	25.0
butane	17.3	nitric oxide	16.3	24.9
butane	18.1	nitrogen dioxide	16.1	24.9
ethylene	17.1	nitric oxide	16.7	25.0
ethylene	17.7	nitrogen dioxide	14.3	25.1
ethylene	18.6	nitrogen dioxide	28.4	25.0
ethylene	31.7	nitrogen dioxide	38.9	25.0
ethylene	43.3	nitrogen dioxide	16.1	25.0
ethylene	44.1	nitrogen dioxide	47.6	25.0

Table 2. Initial conditions for the air oxidation of ppm concentrations of nitric oxide in the presence of various hydrocarbons. (Initial partial pressures of the reactants are given as percentages of the total pressure of the reaction).

Temp (°C)	Total Pressure (mm Hg)	Initial Nitric Oxide (ppm)	Initial Oxygen (percent)	Hydrocarbon	Initial Hydrocarbon (percent)
25.0	766.4	30.7	21.6	none	0.
25.1	756.4	26.2	20.8	none	0.
25.0	766.1	28.7	20.9	methane	0.000097
25.1	768.2	26.9	21.0	methane	0.000981
25.0	771.8	29.4	20.5	methane	0.0118
25.1	764.9	24.4	23.0	methane	0.988
25.3	745.4	37.1	21.6	ethane	0.000105
25.1	761.9	34.7	19.6	ethane	0.00133
25.0	783.4	26.9	21.4	ethane	0.00989
25.1	760.4	29.8	20.8	ethane	0.126
25.0	765.5	39.6	21.9	propane	0.000087
25.2	773.9	28.0	24.8	propane	0.001045
25.2	760.7	38.5	22.8	propane	0.01423
24.9	771.2	31.1	19.1	propane	0.1322
24.8	755.4	26.9	21.9	ethylene	0.000110
25.0	758.9	32.2	20.7	ethylene	0.000976
25.0	765.4	39.4	22.2	ethylene	0.01452
25.0	771.1	43.3	21.7	ethylene	0.1655

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